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THE BECKMANN REARRANGEMENT OF HYDROXAMIC ACIDS

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I. A SINGULAR CASE OF SPONTANEOUS BECKMANN REARRANGEMENT

II. THE MECHANISM OF THE BECKMANN REARRANGEMENT, AND ITS APPLICATION TO HYDROXAMIC ACIDS

I

It is a well known fact that the hydroxamic acids and many of their derivatives are peculiarly susceptible to rearrangements of the Beckmann type. The early investigations of Lossen[1] and his students furnished many striking illustrations of such rearrangements among hydroxamic acids of the aromatic series.

Lossen observed that mono-, di-, and triacylated derivatives of hydroxylamine, upon distillation, all gave rise to isocyanates or their decomposition products, a change which plainly pointed to reactions of the Beckmann type. Thus he[2] found that a monohydroxamic acid decomposed chiefly in accordance with the following equation:

$$R.C(:O)NHOH = R.N:C:O + H_2O = R.NH_2 + CO_2$$

[1] Lossen: Ann. Chem. (Liebig), **161**, 347; **175**, 257; **186**, 1; **252**, 170.
[2] Lossen: *Ibid.*, **175**, 320.

The barium salts,[1] which decomposed even more readily than the monohydroxamic acids themselves, gave aniline, barium carbonate and carbon dioxide. Dihydroxamic acids[2] gave an isocyanate, an acid, an anilide and carbon dioxide:

I. $R.C(:O)NHOCOR' = R.N:C:O + HO.CO.R'$

II. $R.C(:O)NHOCOR' = RNH.CO.R' + CO_2$

The anilide always contained the acid radical which had replaced the hydrogen of the oxime group and the alcohol radical from the other acyl group.

Very interesting results were obtained when the distillation products of triacylhydroxylamines with one anisyl and two benzoyl groups were studied. In terms of the symbols which Lossen[3] employed to designate these compounds, and at the same time to show the order in which the acyl groups successively replaced the hydrogen of hydroxylamine, the three structure isomers with two benzoyl and one anisyl groups were represented as follows (B = benzoyl; A = anisyl):

1. Benzanisbenzhydroxylamine, N.B.A.B.O.
2. Dibenzanishydroxylamine, N.B.B.A.O.
3. Anisdibenzhydroxylamine, N.A.B.B.O.

Upon distillation,[4] these three isomers all gave the same products, but with great variation in the relative proportion of each product:

$$N\left\{\begin{matrix}COC_6H_5\\COC_6H_5\\COC_6H_4OCH_3\end{matrix}\right\}O = \begin{matrix}\text{I. } C_6H_5N:C:O + C_6H_5CO.O.COC_6H_4OCH_3\\ \text{II. } CH_3OC_6H_4N:C:O + (C_6H_5CO)_2O\end{matrix}$$

Lossen[5] showed that the two isomers N.B.A.B.O and N.B.B.A.O gave almost exclusively (90 per cent.) products designated by I in the equation above; while the isomer N.A.B.B.O[6] was decomposed chiefly (75 per cent.) according to II. Later in this article, I shall have occasion to discuss this peculiar behavior from the standpoint of the Beckmann rearrangement.

Furthermore, Lossen and Rothmund[7] showed that potas-

[1] Ann. Chem. (Liebig), **186**, 2 (1877).
[2] Pieschel: *Ibid.*, **175**, 305.
[3] *Ibid.*, **175**, 323.
[4] *Ibid.*, p. 44.
[5] *Ibid.*, p. 21.
[6] *Ibid.*, p. 27.
[7] *Ibid.*, **161**, 359; **175**, 257 (1874).

sium salts of dihydroxamic acids dissolved in boiling water furnished products which can now be accounted for best by assuming a preliminary Beckmann rearrangement. Thus, the potassium salt of the benzoyl ester of benzhydroxamic acid (dibenzhydroxamic acid of Lossen) gave symmetrical diphenylurea, potassium benzoate and carbon dioxide:

$$2C_6H_5C(OK) : NOCOC_6H_5 + H_2O = (C_6H_5NH)_2C : O + KOOCC_6H_5 + CO_2$$

Somewhat later, Thiele and Pickard[1] studied the rearrangement of several dihydroxamic acids and their potassium salts. They made it evident that even in the case of the salts of these acids it is necessary to assume that, in the reaction with water, the final stage must be preceded by a dissociation of the salt into an isocyanate and a potassium salt of the acid related to the acyl group which had replaced the hydrogen of the oxime group:

$$R.C(OK) : NOCOR' = R.N : C : O + KOOC.R'$$

This isocyanate, in the presence of water, would be hydrolyzed, and the amine thus formed would interact subsequently with a second molecule of isocyanate to give a symmetrical disubstituted urea and carbon dioxide:

$$2R.N : C : O + H_2O = (RNH)_2C : O + CO_2$$

They concluded that such a mechanism might be assumed since, with alcohol in place of water, urethanes frequently were formed instead of disubstituted ureas; while in the presence of strong aqueous ammonia, monosubstituted ureas were produced. These compounds would arise naturally by the addition of alcohol or of ammonia to the isocyanate. In this connection it is interesting to note that Stieglitz and Lengfeldt[2] observed that bromoamides, when treated with sodium methylate, gave urethanes.

Phenylacethydroxamic Acid and its Esters.—Among other hydroxamic acids, Thiele and Pickard[3] prepared and inves-

[1] Thiele and Pickard: Ann. Chem. (Liebig), **309**, 189 (1899).
[2] Stieglitz and Lengfeldt: THIS JOURNAL, **18**, 215, 504 (1893).
[3] *Loc. cit.*

tigated phenylacethydroxamic acid (I) and its acetyl ester (II):

$C_6H_5CH_2C(:O)NHOH$ I. $C_6H_5CH_2C(:O)NHO.CO.CH_3$ II.

At the time their results were printed, I was engaged in the preparation of certain hydroxamic acids, among them phenylacethydroxamic acid. Upon the appearance of their article, my work was abandoned. There was, however, one new and particularly interesting observation which I made at that time with the potassium salt of the benzoyl ester of phenylacethydroxamic acid, viz., that in the solid state, at 25°, it spontaneously suffered decomposition and Beckmann rearrangement.[1]

Phenylacethydroxamic acid may be prepared readily in a high state of purity by the action of an alcoholic solution of ethyl phenylacetate upon free hydroxylamine, also dissolved in alcohol. In the course of a few hours the hydroxamic acid separated in large crystals, easily purified by recrystallization from warm ethyl acetate. By the method of Schotten-Baumann, the benzoyl ester of this acid,

$$C_6H_5CH_2C(:O)NHOCOC_6H_5$$

was made. When an alcoholic solution of this ester was treated with the calculated quantity of potassium hydroxide dissolved in alcohol, and sufficient absolute ether was added, a crystalline potassium salt was obtained. This salt, collected rapidly upon a filter, was washed with absolute ether and dried. In the course of a few minutes a dense cloud of white vapor appeared, which sometimes arose with such suddenness that a large vortex ring was sent forth. This vapor consisted entirely of particles of benzyl isocyanate,

$$C_6H_5.CH_2.N:C:O$$

The solid residue which remained scattered upon the support was practically pure potassium benzoate, with a little adhering isocyanate. Even when precautions were taken to exclude moisture during the preparation of the salt, a decomposition

[1] Stieglitz: THIS JOURNAL, **29**, 50 (1903). On the Beckmann Rearrangement. Decennial Publication, University of Chicago, p. 40 (1903).

occurred after the same manner. When one-half gram samples were used, the time intervening between the separation of the salt from ether and alcohol and its decomposition was quite uniform with different samples, and approximated five minutes at ordinary room temperature (25°). These observations clearly indicated a spontaneous decomposition accompanied by Beckmann rearrangement:

$$C_6H_5CH_2C(OK) : NOCOC_6H_5 = C_6H_5CH_2N : C : O + KOOCC_6H_5$$

There are cases on record in which the Beckmann rearrangement of compounds in solution is known to occur with readiness, even at moderately low temperatures. Thus, McCoy and Stieglitz[1] observed that dibromosalicylic bromoamide, with the exceedingly negative radical, $C_6H_2Br_2(OH)$, suffered rearrangement below 5° "in the course of a few seconds, and so rapidly that the bromoamide itself could not be isolated." Van Dam[2] noticed that the same change occurred even at —12°. The azides studied by Curtius[3] were found to undergo the Beckmann rearrangement by loss of nitrogen. Recently, G. Schroeter[4] showed that certain azides (e. g., benzazide and *o*-nitrobenzazide), dissolved in benzene at temperatures ranging from 50°–70°, evolved nitrogen when a stream of carbon dioxide was passed through their solutions; isocyanates in almost quantitative amounts were formed. In the case of the salt under consideration, however, a solid at comparatively low temperature, and in the absence of any solvent or reagent commonly employed to effect rearrangement, gave rise to the usual products of such dissociation.

In a similar manner, certain other salts of hydroxamic acids and of some bromoamides, when heated to temperatures considerably above room temperature, have been observed to decompose explosively. There is not sufficient experimental material at hand to admit of speculation at the present time, but it will be interesting to learn what there

[1] McCoy and Stieglitz: THIS JOURNAL, **31**, 116 (1899).
[2] Van Dam: Rec. trav. chim., **18**, 108 (1899); **19**, 318 (1900).
[3] Curtius: J. prakt. Chem., **63**, 428 (1901). Ber. d. chem. Ges., **35**, 3229 (1902).
[4] Schroeter: Ber. d. chem. Ges., **42**, 2336 (1911).

is in the nature of this particular compound which makes it so sensitive to rearrangement, while other compounds with similar constitutional formulae appear to be markedly more stable. Thus, the sodium salt of the benzoyl ester of phenylacethydroxamic acid does not decompose suddenly, but changes very slowly in the course of many days. Even after several hours the potassium salt of the acetyl ester of phenylacethydroxamic acid showed no tendency to decompose at 25°. At 50°, however, it puffed suddenly after four or five minutes.

EXPERIMENTAL PART

Phenylacethydroxamic Acid

By the action of hydrogen sulphide upon the copper salt suspended in dry alcohol and ether, Thiele and Pickard[1] obtained phenylacethydroxamic acid, which they describe as a solid melting at 121°. I have found it preferable to prepare the acid by causing ethyl phenylacetate to react with free hydroxylamine.

Forty grams of ethyl phenylacetate were mixed with ten grams of hydroxylamine and enough ethyl alcohol to yield a homogeneous solution. In the course of a few hours, a sample of the solution gave a decided color test with ferric cloride, showing the presence of hydroxamic acid, but it required about four days to complete the reaction. During this time, phenylacethydroxamic acid crystallized from the solution in coarse needles or sometimes in large transparent plates. After the separation of the crystals, the mother liquid was evaporated and yielded more of the acid. In all, about 35 grams were obtained.

Warm ethyl acetate was found to be the best solvent, and was employed in purifying the acid. It could also be crystallized from a solution in boiling water. It was soluble in warm alcohol, but only sparingly soluble in ether or in ligroin. The melting point was found to be 145°–145°.5 with some decomposition.[2].

[1] Thiele and Pickard: Ann. Chem. (Liebig), **309**, 201 (1899).

[2] Thiele and Pickard (*loc. cit.*) recorded the melting point as 121°. I have never obtained a sample of the acid which melted at 121°. I was at first inclined to think that the melting point given by Thiele and Pickard might be a misprint; but the fact

An analysis of the acid melting at 145°–145°.5 gave the following values:

0.1814 gram substance gave 15.4 cc. N at 24° and 740.8 mm.

0.1214 gram substance gave 0.2836 gram CO_2 and 0.0675 gram H_2O.

	Calculated for $C_8H_9O_2N$	Found
C	63.58	63.71
H	5.96	6.17
N	9.27	9.33

The Benzoyl Ester of Phenylacethydroxamic Acid
$C_6H_5CH_2CONH(OCOC_6H_5)$

The benzoyl ester was made either by fusing the hydroxamic acid with benzoic anhydride (1), or by the Schotten-Baumann method (2).

Method (1).—Eight grams of phenylacethydroxamic acid, mixed with a slight excess of benzoic anhydride, were fused at 120° until a sample of the product, when dissolved in water, gave no color test with ferric chloride. After the crude product had been broken up and extracted repeatedly with ligroin to remove benzoic acid and any unchanged benzoic anhydride, the remaining solid was dissolved in boiling alcohol, and hot water was added until the solution became slightly turbid. This solution, upon cooling, deposited brilliant colorless needles of the ester.

Method (2).—When the Schotten-Baumann method was employed, the ester was made as follows: Ten and one-half grams of the acid were dissolved in 100 cc. of water and 4 grams of potassium hydroxide were added. Considerable heat was evolved, and after a few minutes a dense precipitate separated. The shaking of the mixture was continued until the odor of benzoyl chloride had practically disappeared. The crude product was then collected, dried, extracted with ligroin, and recrystallized in the manner described above.

that the acetyl ester prepared by Thiele and Pickard melted at 121°, while the acetyl ester which I have made repeatedly melted at 148°–149° would lead to the conclusion that two distinct isomeric phenylacethydroxamic acids have been under investigation in the two instances.

The benzoyl ester melted at 120°.5–121°.5 with indications of fusion at 118°. When it was heated to a temperature slightly above its melting point, the odor of isocyanate became distinctly noticeable at once. The ester was almost insoluble in water and in ligroin. It was only sparingly soluble in ether, but quite readily in warm alcohol.

An analysis gave the following value for nitrogen:

0.338 gram substance gave 16.75 cc. N at 14° and 738.2 mm.

	Calculated for $C_{15}H_{13}O_3N$	Found
N	5.49	5.67

Potassium Salt.—Two grams of the benzoyl ester were dissolved in alcohol and a solution of 0.45 gram of potassium hydroxide was added. The mixture became warm, but no precipitate was formed until ether was added, which caused the tardy separation of a white crystalline salt, heavy and granular in appearance.

This salt was collected upon a filter, and after it had been washed rapidly with ether it was placed upon a porous support to dry. In the course of several minutes, sudden decomposition occurred, in all cases accompanied by a hissing sound and a dense cloud of the vapor of benzyl isocyanate; potassium benzoate remained as a solid residue. The identity of the isocyanate was established by passing the vapor into water, with which it reacted to give symmetrical dibenzylurea,

$$(C_6H_5CH_2.NH)_2CO$$

a solid melting at 169°, identical with a sample of symmetrical dibenzylurea made for comparison. When the solid residue left by the decomposition was dissolved in water, a slight amount of symmetrical dibenzylurea, caused by adhering isocyanate, separated and was removed. Dilute hydrochloric acid added to the filtrate gave crystals of benzoic acid which melted at 121°.

To make sure that the decomposition was not caused by moisture absorbed from the air, precautions were taken to prepare the salt in such a way that moisture was excluded as

thoroughly as possible. The salt was collected upon a filter placed under a bell jar through which dry air was passing, and was transferred at once to a desiccator. In the course of five or six minutes, decomposition ensued as before; the force of the decomposition was sufficient to lift the cover of the desiccator and throw it upon the table.

At 0° the salt was comparatively stable. A sample was kept for several hours in a tube surrounded by ice. When, however, it was transferred to a crucible for weighing, it decomposed suddenly before the weighing could be completed.

When the salt, immediately after preparation, was dissolved in cold water, a clear solution was obtained. But if a minute or two had elapsed before the salt was treated with water, a turbid solution invariably resulted. When the clear solution was boiled, a dense crystalline precipitate quickly separated. This was shown to be symmetrical dibenzylurea; it melted at 169°.

An analysis of the potassium salt gave the following value for potassium:

0.5143 gram substance gave 0.1515 gram K_2SO_4.

	Calculated for $C_{15}H_{12}O_3NK$	Found
K	13.33	13.21

Sodium Salt.—The calculated amount of sodium hydroxide dissolved in alcohol was added to an alcoholic solution of the benzoyl ester. The bulky, gelatinous precipitate thrown out by ether was collected and washed with ether. At ordinary room temperature the salt, even after two hours, showed no indications of decomposition; there was no noticeable odor of isocyanate, and the salt gave a clear solution in cold water. When the salt was heated, it puffed and gave benzyl isocyanate.

Analysis:

0.2639 gram substance gave 0.0674 gram Na_2SO_4.

	Calculated for $C_{15}H_{12}O_3NNa$	Found
Na	8.30	8.27

Silver Salt.—By the action of silver nitrate upon a fresh solution of the potassium or the sodium salt, a white precipi-

tate was formed. The silver salt was apparently more stable than either of the other salts. When it was heated on a spatula over the flame it decomposed. A small sample (0.1 gram) in a test tube finally puffed after it had been heated for several minutes at a temperature of 70°.

Acetyl Ester of Phenylacethydroxamic Acid

$C_6H_5.CH_2CO.NH(O.COCH_3)$

Five grams of phenylacethydroxamic acid (melting at 145°–145°.5) were heated with an equal weight of acetic anhydride until a sample of the mixture, when dissolved in water, showed no color reaction with ferric chloride. Considerable heat was evolved during the reaction, and the mixture solidified partially upon cooling. After the product had been dried, it was recrystallized from warm ethyl acetate, from which it separated in long flat crystals which melted at 148°–149°. The ester may be crystallized from alcohol. It is almost insoluble in water and in ligroin, and only sparingly soluble in boiling ether.

Analysis:

0.3279 gram substance gave 22.3 cc. N at 29° and 743.3 mm.

	Calculated for $C_{10}H_{11}O_3N$	Found
N	7.25	7.28

Potassium Salt.—One gram of the acetyl ester was dissolved in alcohol and mixed with an alcoholic solution of potassium hydroxide (1 molecule), but the solution remained clear until ether was added. This caused the salt to separate as a voluminous white precipitate. The salt was washed with ether and dried in a desiccator. It showed no inclination to decompose after the fashion of the potassium salt of the benzoyl ester. However, when a sample (0.1 gram) placed in a test tube was heated in a bath to 70°, it puffed in about two minutes; at 50°, the time required was about six minutes. At room temperature (25°) after two hours there was no visible sign of change; the salt was still completely soluble in water and possessed no odor of isocyanate.

When a water solution of the salt was boiled, symmetrical

dibenzylurea was formed, but somewhat more slowly than with the potassium salt of the benzoyl ester. A white silver salt was precipitated upon the addition of silver nitrate to a solution of the sodium salt.

Other Esters of Phenylacethydroxamic Acid

By the action of various acid anhydrides upon phenylacethydroxamic acid, the following esters were prepared: propionyl ester, melting at 138°–139°; normal butyryl ester, melting at 113°–114°; isobutyryl ester, melting at 111°–112°.

II

A. Mechanism of the Beckmann Rearrangement

Since the announcement by Beckmann[1] in 1886 of the singular rearrangement of certain oximes in the presence of phosphorus pentachloride, there has been, perhaps, no other one class of rearrangements among organic compounds which has led to so much investigation. Still, at the present time, it can hardly be said that chemists have reached any unanimity concerning appropriate symbols by which to portray the mechanism of this rearrangement.

The evidence, as I view it, seems to favor the position held by Stieglitz,[2] viz., that the prime factor leading to such rearrangement consists in a dissociation accompanied by a change in valence of the nitrogen atom from three to one, with subsequent readjustment of the groups induced by the presence of univalent nitrogen:

$$R.C(:O)N\begin{matrix}X\\Y\end{matrix} \longrightarrow R.C(:O)N< + XY \longrightarrow R.N:C:O + XY$$

Evidence has accumulated to establish the fact that the Beckmann rearrangement occurs readily when conditions arise which make it possible by an inspection of the constitutional formulas of certain classes of compounds to predict for nitro-

[1] Beckmann: Ber. d. chem. Ges., **19**, 988 (1886); **20**, 1507, 2508 (1887). Hofmann: *Ibid.*, **14**, 2725 (1882); **15**, 408 (1883).

[2] J. Stieglitz: This Journal, **18**, 751 (1896); **29**, 49 (1903). Stieglitz and Earl: *Ibid.*, **30**, 399, 412 (1903). Stieglitz and Slosson: Ber. d. chem. Ges., **28**, 3266 (1896) **34**, 1613 (1902). Slossen: This Journal, **29**, 289 (1903).

gen a change of valence of this kind. Furthermore, rearrangement fails to take place when such conditions are not apparent, or easily realizable by the assumption of plausible intermediate reactions with reagents employed to bring about rearrangement.

Among the many convincing arguments brought forward by Stieglitz in support of his interpretation, the following may be mentioned as probably of the most weight:

(1) Stieglitz[1] has shown that certain stereoisomeric (*syn* and *anti*) halogen imido esters do not undergo the Beckmann rearrangement even when heated to 150°. This fact leads to the conclusion that the presence of a [illegible] nitrogen cannot be the only determining factor, [illegible] not the only determining factor, as Hantzsch[2] and [illegible]ntz and Peterson,[3] [illegible]etones,

[illegible] not rearrange [illegible]. [illegible] assumption that [illegible] products in the rearrangement [illegible] tion was made by Hantzsch.[4]

(2) According to the [illegible] and van Dorp,[5] rearrangement occurs with salts of bromoamides by virtue of the tendency of nitrogen to combine with radicals more positive than the halogens:

$$\begin{array}{l} R-C:O \\ \quad | \\ Br-N-K \end{array} \longrightarrow \begin{array}{l} Br-C:O \\ \quad | \\ R-N-K \end{array}$$

Contrary to this assumption, however, it has been shown that of two bromoamides the salt of the one with the more negative group often shows rearrangement with the greater readi-

[1] Stieglitz: THIS JOURNAL, **40**, 36 (1908). Hilpert: *Ibid.*, **40**, 155 (1908).
[2] Hantzsch: Ber. d. chem. Ges., **35**, 3579 (1902).
[3] *Ibid.*, **42**, 782 (1900).
[4] *Ibid.*, **24**, 3516 (1891).
[5] Hoogewerff and van Dorp: Rec. trav. chim., **6**, 373 (1887); **8**, 173 (1889), etc.

ness. This is illustrated in a striking manner by the behavior of the bromoamide of dibromosalicylic acid mentioned on page 5. Then again, β-phenyl-β-benzoylhydroxylamine,[1]

$$C_6H_5N(COC_6H_5)OH$$

under the influence of reagents usually employed to bring about rearrangement, does not give rise to any product of that character; not a trace of diphenylamine could be detected, "and yet the color tests for this substance belong to the most sensitive known to organic chemistry."[2] It is interesting in this connection to consider the behavior of the potassium salt of the benzoyl ester of benzhydroxamic acid, which easily undergoes rearrangement:

$$\begin{array}{l} C_6H_5-C:O \\ \qquad\quad | \\ C_6H_5CO-O-N-K \end{array}$$

Furthermore, it has been shown that bromoalkylamides,

$$\begin{array}{l} R-C:O \\ \quad\ | \\ Br-N-R' \end{array}$$

do not rearrange,[3] although, on the assumption of Hoogewerff and van Dorp there is no apparent reason why such compounds should not do so.

(3) The interpretation offered by Stieglitz is the only one which, in an unconstrained way, can explain the decomposition and rearrangement of azides and diazides:[4]

$$C_6H_5.C(:O)N\begin{array}{l}N \\ \| \\ N\end{array} \longrightarrow C_6H_5.C(:O)N< + N_2 \longrightarrow$$

$$C_6H_5.N:C:O + N_2$$

(4) Perhaps the most convincing argument is to be found in the behavior of triphenylmethylhydroxylamine, which has been shown by Stieglitz[5] to suffer the Beckmann rearrangement when the usual reagents are allowed to act upon it:

$$(C_6H_5)_3C.NHOH \longrightarrow (C_6H_5)_3C.N< + H_2O \longrightarrow$$

$$(C_6H_5)_2C:NC_6H_5 + H_2O$$

[1] Stieglitz: THIS JOURNAL, **29**, 53 (1903).
[2] *Ibid.*, **29**, 53 (1903).
[3] *Ibid.*, **29**, 289 (1903).
[4] Curtius: *Loc. cit.* Schroeter: Ber. d. chem. Ges., **44**, 1207 (1911).
[5] Stieglitz: *Ibid.*, **46**, 327 (1911), note.

Benzophenone phenylimide was formed, and its presence was established by hydrolysis; it gave benzophenone and aniline.

Unless we wish to claim that in the final analysis the different classes of compounds which show molecular rearrangements up to this time regarded as belonging to the Beckmann type may yield similar products by reactions essentially different in kind, it would seem to me that the evidence presented above is convincing enough to force upon us the conclusion of Stieglitz, that the predisposing cause is to be sought in the potency of the free valences of *univalent nitrogen*; at least, this hypothesis has offered a mechanism which explains most of the known facts, and does so in a manner less constrained than any other proposed interpretation has yet succeeded in doing.

B. Application to Hydroxamic Acids

Amides.—In applying this viewpoint to the rearrangement of hydroxamic acids, certain characteristic properties of the amides may be considered first, since our present modes of formulating the reaction of the hydroxamic acids are largely based upon analogies drawn from these compounds.

In the case of amides and monohalogen amides, many investigations, chemical as well as physical-chemical in character, have shown that they are unquestionably tautomeric in chemical behavior. In no single instance, however, have chemists succeeded in isolating the two isomeric amides which structure chemistry predicts. Hantzsch[1] pointed out that neither the amides nor their salts will give color reactions with ferric chloride, and that they do not react with phenyl isocyanate. On the other hand, Buehner[2] showed that, by the action of dimethyl sulphate, some amides can be converted into imido esters. Thus, benzamide was changed into the methyl sulphate derivative of its methyl imido ester to the extent of 90 per cent. Similar results have been obtained with diazomethane. Hantzsch and Dollfus[3] concluded that the halogen amides, R.CO.NH(Hal), were to be regarded as pseudo acids because of their behavior with ammonia in various or-

[1] Hantzsch: Ann. Chem. (Liebig), **296**, 90 (1897).
[2] Buehner: *Ibid.*, **333**, 289 (1904).
[3] Hantzsch and Dollfus: Ber. d. chem. Ges., **35**, 228, 250 (1902).

ganic solvents (Hantzsch's "ammonia reaction" for pseudo acids). This method,[1] however, has lost much of the certainty ascribed to it originally.

Although the salts of amides have been generally assigned imido salt formulas, R.C(OMe) : NH, there is, perhaps, at present more diversity of opinion on this point than ever before. Long ago the inconsistency of assuming that the alkali or the silver salts of such substances as nitrous, sulphurous, hydrocyanic acids, ethyl acetoacetate, etc., were mixtures of two independent isomeric salts in a definite fixed ratio became apparent to all; for the amounts of two isomeric derivatives formed by the interaction of a reagent with any one of these salts was not fixed, but varied with the reagent employed, as well as with the alterable physical conditions of the experiment.

Investigation showed that rearrangements of alkyl and acyl derivatives of these acids frequently occurred under the influence of heat or certain chemical reagents. Thus isonitriles passed into nitriles; symmetrical esters of sulphurous acid into sulphonic acids; esters of thiocyanic acid into mustard oils; O-derivatives of ethyl acetoacetate into C-derivatives. Even in the case of the silver and alkali salts of the amides, at first thought to give oxygen-alkyl or nitrogen-alkyl derivatives, respectively, the experiments of Comstock and Wheeler[2] and later of other investigators tended to confirm the belief that neither the alkali nor the silver salt gave exclusively one type of alkyl isomer, but that, depending upon temperature and the presence of an excess of reagent (e. g., halogen alkyl[3]), the oxygen ester first formed seemed to suffer rearrangement to give the nitrogen-alkyl isomer. So that, notwithstanding the simultaneous formation of two isomers, the belief remained practically unshaken that all of the salts of amides were to be represented by formulas with the metal bound to oxygen.

On the other hand, there appeared to be evidence, fragmentary to be sure, which pointed to the existence of salts

[1] Hantzsch: Ber. d. chem. Ges., **40**, 3804 (1907). Michael: *Ibid.*, 4380, 4916 (1907).

[2] Comstock and Wheeler: THIS JOURNAL, **13**, 522 (1891).

[3] Wheeler: *Ibid.*, **21**, 185 (1899); **23**, 140 (1901).

which must be represented by formulas in which the metal was bound to nitrogen. Thus, Ley and Kissel[1] inferred from the electrical conductivity and chemical behavior of mercury acetamide that it more probably should be represented by the amide formula, $Hg(NH.CO.CH_3)_2$. Schroeter[2] is inclined to represent bromoamide salts by formulas with sodium bound to nitrogen, R.CO(NBrNa). He assumed that the decomposition of these salts, with loss of sodium bromide and rearrangement, would be more satisfactorily pictured by this formula in terms of the views which Stieglitz holds concerning the Beckmann rearrangement. By the action of solutions of mercuric salts upon solutions of trisodium cyanurate at 0° and at 100°, Hantzsch[3] obtained two isomeric mercury salts totally different in chemical behavior. At 0°, a salt which Hantzsch represented by the formula $(CN)_3(OHg)_3.2H_2O$ was obtained. At 100° the isomeric salt $(CO)_3(NHg)_3.H_2O$ resulted. Both salts could be dehydrated without decomposition. These salts would therefore correspond to the amide and the imide salt forms,

$$-C(O\,Hg):N- \qquad\qquad -C(:O)N\,Hg-$$

Those who clung to the oxygen theory of the salts were forced to seek some mechanism whereby two isomers might be formed simultaneously or the isomer with the group bound to oxygen might be transformed into the modification with the same group linked to nitrogen. The rearrangement was explained by Wheeler[4] as a process of addition in which the halogen alkyl united with the imido ester in such a way that the alkyl group attached itself to nitrogen and the halogen to carbon. Exception has been taken to this mechanism by Brunel and Acree,[5] who point out that "the fact that rearrangement may take place is no proof that it alone is accountable for the formation of two products." In the alkylation experiments with urazole salts, which they carried out quantitatively under varying conditions, for each salt a mixture of

[1] Ley and Kissel: Ber. d. chem. Ges., **32**, 1358 (1899).
[2] Schroeter: *Ibid.*, **43**, 2337 (1910).
[3] Hantzsch: *Ibid.*, **35**, 2718 (1902).
[4] Wheeler: THIS JOURNAL, **21**, 187 (1899).
[5] Brunel and Acree: *Ibid.*, **43**, 512 (1910).

oxygen-alkyl and nitrogen-alkyl derivatives was formed in practically constant ratio. If the oxygen ester had rearranged to give the nitrogen ester, the ratio of the amounts of these two esters should have varied with the time of reaction, etc., but no such variation was observed by Brunel and Acree.

Michael[1] and others sought to account for the two forms by assuming that the oxygen ester was produced by the direct replacement of the metal, while the nitrogen derivative was obtained by the addition of the reagent to the double bond between nitrogen and carbon, with subsequent loss of a salt.

Another device, the rearranged anion, has been used by several investigators (Nef, Lapworth, and others)[2] although the scheme tacitly is almost, if not quite, an admission of the existence of salts in tautomeric equilibrium. It at least presupposes the existence of tautomeric anions in equilibrium, and unless the salts to which these anions belong are dissociated to an infinite degree, a certain per cent. of the two corresponding tautomeric salts must be present in the system too.

Acree and his collaborators,[3] in a study of the urazole and thiourazole salts, have not hesitated to assume the existence of tautomeric salt isomers and anions in equilibrium, and have published quantitative results which seem to verify their conclusions. These salts would correspond to the amide and imide forms:

$$—C(:O)NNa— \qquad —C(ONa):N—$$

It is quite probable that in the future two distinct modifications (salt isomers) of the salts of amides will be isolated; possibly the orange and white silver salts of different stabilities already isolated[4] in certain cases may represent such isomers.

Monohydroxamic Acids.—The monohydroxamic acids pre-

[1] Michael: J. prakt. Chem., **37**, 469; **45**, 580; **46**, 189, etc. THIS JOURNAL, **43**, 322. Ber. d. chem. Ges., **43**, 621. Nef: Ann. Chem. (Liebig), **266**, 52; **276**, 200; **277**, 59, 83; **298**, 263, etc.

[2] Nef: Ann. Chem. (Liebig), **309**, 157, 158 (1899). Lapworth: J. Chem. Soc., **81**, 1503 (1902); **83**, 1121 (1903); **85**, 30 (1904).

[3] Acree: THIS JOURNAL, **38**, 1; **39**, 125, 226. Ber. d. chem. Ges., **41**, 3199. Nirdlinger and Acree: THIS JOURNAL, **43**, 358 (1910). Brunel and Acree: *Ibid.*, **43**, 517 (1910).

[4] Titherley: J. Chem. Soc., **71**, 466 (1898); **79**, 408 (1901).

sent a possibility of tautomerism very similar to that proposed for amides. No agreement concerning the formula of the free hydroxamic acids has yet been reached. Possibly because of the stereoisomeric relations observed in the case of certain esters, R.C(OR') : NOH, preference has usually been given to the hydroximic form, R.C(OH) : NOH, although no valid experimental objection can be raised against the hydroxamic formula, R.C(: O)NHOH. The hydroxamic formula would more naturally express the decomposition according to the view of Stieglitz:

$$RC(:O)NHOH \longrightarrow R.C(:O)N< + H_2O \longrightarrow$$
$$R.N:C:O + H_2O \longrightarrow RNH_2 + CO_2$$

In the case of formhydroxamic acid, at least, the hydroxamic formula is the more plausible by far, since it accounts for the fact that formhydroxamic acid and its salts do not yield fulminic acid or fulminates,[1] as they would be expected to do very readily if the hydroximic formula were chosen for them:

$$HOHC:NOH \longrightarrow HOH + >C:NOH$$

Instead of these products, formhydroxamic acid, upon dissociation, readily gives carbon monoxide and hydroxylamine,[2] a reaction which was found by me to be slightly reversible:[3]

$$\begin{matrix} HOHN \\ \\ H \end{matrix}\!\!\diagup C:O \rightleftharpoons H_2NOH + CO$$

Furthermore, in the presence of alkalies it undergoes the Beckmann rearrangement, and yields carbonates and ammonia:[4]

$$H.C(:O)NHOH \longrightarrow H.C(:O)N< + H_2O \longrightarrow$$
$$H.N:C:O + H_2O \longrightarrow NH_3 + CO_2$$

The Dihydroxamic Acids.—The acyl esters of monohydroxamic acids (dihydroxamic acids) have been regarded as tautomeric in behavior and, so far as evidence goes, may be represented by the two formulas:

$$RC(:O)NHOCOR' \qquad RC(OH):NOCOR'$$

[1] Jones: THIS JOURNAL, **20**, 27–32 (1898). Biddel: Ann. Chem. (Liebig), **310**, 13 (1900).

[2] Jones, Biddell: *Loc. cit.*

[3] Jones and Oesper: THIS JOURNAL, **42**, 516 (1909).

[4] Wieland: Die Knallsäure, p. 32 (1909).

The former would lend itself to an interpretation of the rearrangement in accordance with the theory of Stieglitz, and would thus explain the ease with which a dihydroxamic acid upon distillation gives a fatty acid, an isocyanate, an anilide and carbon dioxide:

$$R.C(:O)NHOCOR' \longrightarrow R.C(:O)N< + HOOC.R' \longrightarrow R.N:C:O + HOOC.R'$$

Of course, if the hydroximic formula is considered, it will be apparent that there would be no inconsistency in assuming a loss of acid, HOC(: O)R.

The Salts of Dihydroxamic Acids.—Similar to the salts of bromoamides, these salts have usually been represented by hydroximic formulas:

$R.C(OMe):NOCOR'$	$R.C(:O)NMe.OCOR'$
Hydroximic Formula	Hydroxamic Formula

Schroeter[1] has ventured to propose that the metal might be linked to nitrogen, and has suggested that this formula would lend itself more readily to the interpretation of the rearrangement of these salts in accordance with Stieglitz's view of the Beckmann rearrangement.

Evidence of the existence of tautomeric salt isomers among these salts is suggested by experiments which I carried out in 1897.[2] By the action of benzoyl chloride upon the sodium salt of the benzoyl ester of acethydroxamic acid,

$$CH_3C(:O)NNa.OCOC_6H_5$$

two compounds were formed: a solid melting at 68–69°, and an oil. This solid was shown to be α-benzoyl-β-acetylbenzoylhydroxylamine, a real triacylated hydroxylamine,[3]

$$CH_3C(:O)N(COC_6H_5)OCOC_6H_5$$

The sufficiency of this formula was established by two methods. In the first place, upon alcoholysis[4] with alcoholic potash the solid (melting at 68°–69°) gave exclusively the

[1] Schroeter: Ber. d. chem. Ges., **44**, 1201 (1911).
[2] Jones: THIS JOURNAL, **20**, 13 (1898).
[3] Jones: *Loc. cit.*, p. 15.
[4] *Loc. cit.*, p. 15.

benzoyl ester of benzhydroxamic acid (dibenzhydroxamic acid),

$$C_6H_5C(:O)NH(OCOC_6H_5)$$

and ethyl acetate. *Not a trace of the benzoyl ester of acethydroxamic acid,*

$$CH_3.C(:O)NH(OCOC_6H_5)$$

could be found. The oil[1] which accompanied this solid was hydrolyzed and gave the benzoyl ester of acethydroxamic acid and ethyl benzoate almost exclusively. This oil, therefore, consisted almost entirely of the O-isomer, the benzoyl ester of benzoylacethydroximic acid,

$$CH_3C(OCOC_6H_5) : NOCOC_6H_5$$

In the second place, the same solid compound (melting at 68°–69°) was made by the action of acetyl chloride upon the potassium salt of the benzoyl ester of benzhydroxamic acid,

$$C_6H_5C(:O)NK — OCOC_6H_5$$

The identity[2] of the two substances was established by the fact that both gave the same products upon alcoholysis, by a crystallographic comparison of the crystals, and by the constancy of the melting point of a mixture of crystals prepared in the two ways. An O-isomer formed in this second reaction,

$$C_6H_5C(OCOCH_3) : NOCOC_6H_5$$

was a solid melting at 84°–85°. Upon alcoholysis it gave the benzoyl ester of benzhydroxamic acid and ethyl acetate.

From the standpoint of tautomeric salts, the formation of an identical product in the two cases would be explained by the presence of the two nitrogen salt isomers:

$$CH_3C(:O)NK.OCOC_6H_5 \qquad C_6H_5C(:O)NK.OCOC_6H_5$$
$$\text{I} \qquad\qquad \text{II}$$

The first salt with benzoyl chloride would plainly yield the same compound which the second salt would give when acted upon by acetyl chloride, viz.,

$$CH_3C(:O)N(COC_6H_5).OCOC_6H_5$$

Since these experiments were largely qualitative in character, the proposed interpretation is based chiefly upon analogy,

[1] *Loc. cit.*
[2] Jones: *Loc. cit.*

and until quantitative results are obtained it will not be possible to state positively that the reactions could not be accounted for by a rearrangement of the O-acyl to the N-acyl compound, a reaction which seems to play a role in certain reactions of the triacylated hydroxylamines.

A possible interpretation of the singular behavior of the potassium salt of phenylacethydroxamic acid benzoyl ester described above may be deduced from a tautomeric equilibrium between two salts:

$$C_6H_5CH_2C(OK) : NOCOC_6H_5 \rightleftharpoons C_6H_5CH_2C(:O)NK.OCOC_6H_5$$

If this reaction is assumed to proceed from left to right with a measurable velocity, and if the form on the right should dissociate into an isocyanate and potassium benzoate, there may be an autocatalytic effect which accelerates the reaction from left to right; or, because of the suppression of the one form by dissociation and Beckmann rearrangement, the reaction, at the proper temperature, of its own accord may proceed with sufficient velocity to permit the heat evolved to more than counterbalance that lost by conduction and otherwise, so that the action may soon reach the violence of an explosion. The phase of the reaction is now being investigated.

Triacyl Derivatives of Hydroxylamine.—The explanation of the products formed by the rearrangement of triacylated hydroxylamines is a much more complicated problem. The conclusions reached in the preceding section of this paper make it evident that each triacylated hydroxylamine may exist in two isomeric structure forms, as well as in several polymorphous modifications.[1]

In proposing a hypothesis to account for the behavior of these compounds it is significant to note that rearrangements among O-acyl compounds have been reported frequently. Thus, Werner and Skiba[2] showed that the benzoyl ester of

[1] Lossen: *Loc. cit.*

[2] Werner and Skiba: Ber. d. chem. Ges., **27**, 2198 (1894); **32**, 1654 (1899). In most cases two products were formed, viz., the acylhydroxamic acid and a dioximehyperoxide, RC(=N—O—O—N)CR′.

benzhydroximic acid, a solid melting at 95°, could be kept only a short time, since it rapidly rearranged to give dibenzhydroxamic acid:

$$C_6H_5C(OCOC_6H_5) : NOH \longrightarrow C_6H_5C(: O)NHOCOC_6H_5$$

The same tendency to rearrange was manifested by other acyl derivatives, such as the *m*-chlorobenzoyl, *m*-nitrobenzoyl, *p*-nitrobenzoyl esters, etc.; in some cases it was impossible to isolate the acyl hydroximic acid. Similarly, attempts to make acyl imido esters[1] have led invariably to the formation of diamides by rearrangement:

$$RC(OCOR) : NH \longrightarrow RC(: O)NHCOR$$

In the destructive distillation of triacylated hydroxylamines, it would be reasonable to assume that similar rearrangements may occur, and this seems necessary if the products actually formed are to be accounted for. Steiner[2] showed that tribenzoylhydroxylamine upon distillation was almost completely dissociated into phenyl isocyanate and benzoic anhydride. If this triacyl derivative is not a real hydroxylamine but its tautomer, the probability that it will change to the hydroxylamine form upon distillation seems very great. Upon this assumption the following reactions would occur:

$$C_6H_5C(OCOC_6H_5) : NOCOC_6H_5 \longrightarrow$$
$$C_6H_5C(: O)N(COC_6H_5)OCOC_6H_5 \longrightarrow$$
$$C_6H_5C(: O)N< + (C_6H_5.CO)_2O \longrightarrow$$
$$C_6H_5N : C : O + (C_6H_5CO)_2O$$

When, however, the products formed by the distillation of the isomeric hydroxylamine derivatives with two benzoyl and one anisyl group are inspected, it will be clear that even the shifting of the acyl groups from O to N cannot logically account for the fact that, by dissociation and rearrangement, benzanisbenzhydroxylamine (N.B.A.B.O) decomposed to the extent of 10 per cent. into *p*-methoxyphenyl isocyanate and benzoic anhydride. Furthermore, since dibenzanishydroxylamine (N.B.B.A.O) and anisdibenzhydroxylamine (N.A.B.B.O)

[1] Pinner: Ber. d. chem. Ges., **25**, 1434 (1892).
[2] Steiner: Ann. Chem. (Liebig), **178**, 225 (1875).

by a shifting of an acyl group from O to N should yield the same hydroxylamine derivative, viz.,

$$C_6H_5C(:O)N(COC_6H_4OCH_3)OCOC_6H_5$$

it is not plain why the dibenzanishydroxylamine should yield phenyl isocyanate and benzoylanisyl oxide to the extent of 90 per cent. (p. 2), while anisdibenzhydroxylamine should yield only 25 per cent. (p. 2) of the same products.

A possible interpretation of the formation of *p*-methoxyphenyl isocyanate may be found in the following assumption: Upon decomposition benzanisbenzhydroxylamine should undergo the following changes:

$$C_6H_5C(OCOC_6H_5):NOCOC_6H_4OCH_3 \longrightarrow$$
$$C_6H_5C(:O)N(COC_6H_5)OCOC_6H_4OCH_3 \longrightarrow$$
$$C_6H_5C(:O)N< + C_6H_5CO.O.COC_6H_4OCH_3 \longrightarrow$$
$$C_6H_5.N:C:O + C_6H_5CO.O.COC_6H_4OCH_3$$

It may be assumed that the intermediate product, $C_6H_5CON<$, before rearrangement may interact by addition in two different ways with the recently formed anhydride. In the first place, the original triacylhydroxylamine would be formed; in the second place, an isomer,

$$C_6H_5C(:O)N(COC_6H_4OCH_3)OCOC_6H_5$$

This form, by loss of benzoic anhydride and Beckmann rearrangement, would give *p*-methoxyphenyl isocyanate.

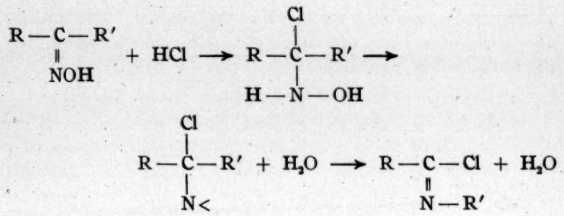
The second difficulty mentioned above furnishes the most serious objection, and so far as I can see no satisfactory explanation of it can be given in the language of the hypothesis. One might imagine that during the process of rearrangement of the O-acyl to the N-acyl derivative, a condition favoring the loss of a particular anhydride (e. g., anisyl benzoyl oxide in the case of dibenzanishydroxylamine), might exist, so that in this instance an excess (90 per cent.) might be found to dissociate into phenyl isocyanate; but this proposal savors too much of calling in the Nascent State to help out.

C. Stereoisomers and the Beckmann Rearrangement

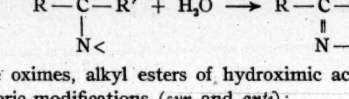
From the standpoint of stereoisomerism the hypothesis of Stieglitz does not seem to form a complete picture of the

mechanism of the Beckmann rearrangement, and it is in this field that it has met with the most criticism.[1]

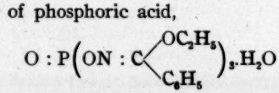
To account for the Beckmann rearrangement of oximes in terms of his hypothesis, Stieglitz[2] was forced to assume the addition of some reagent, HX (e. g., hydrogen chloride), to the double bond between nitrogen and carbon; then the subsequent loss of water would lead to univalent nitrogen and the accompanying rearrangement:



Like the oximes, alkyl esters of hydroximic acids exist in stereoisomeric modifications (*syn* and *anti*):



Werner[3] found that with phosphorus pentachloride one of these isomers suffered the Beckmann rearrangement, while the second isomer under similar treatment showed no inclination to take part in such a rearrangement, but gave instead a complex ester of phosphoric acid,



One cannot avoid surprise that a single isomer and not both should undergo rearrangement, provided the presence of univalent nitrogen alone determines the possibility of such rearrangement, since the addition of hydrogen chloride would be

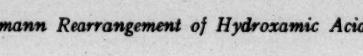
[1] Montagne: Ber. d. chem. Ges., **43**, 2014 (1910).

[2] Stieglitz: This Journal, **18**, 751 (1896), note. Stieglitz and Peterson: Ber. d. chem. Ges., **43**, 784 (1910). Schroeter: *Ibid.*, **44**, 1207 (1911). Nef: This Journal, **18**, 753 (1896).

[3] Werner: Ber. d. chem. Ges., **25**, 33 (1892); **26**, 1562 (1893); **29**, 1153 (1896).

expected to occur equally well in the case of each isomer if stereoisomeric relations exert no modifying influence to prevent it.

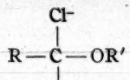
Then again, it would seem probable that the stereoisomeric chloroimido esters,



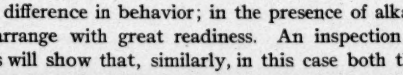
studied by Stieglitz,[1] might have rearranged, provided this rearrangement may be induced by the addition of hydrogen chloride to the double bond, while, as a matter of fact, a totally different reaction occurred:

$$R.C(OR) : NCl + 2HCl \longrightarrow R.C(OR) : NH.HCl + Cl_2$$

Of course, in this case, it must be assumed that the specific character of hypochlorous chlorine (Cl^+)[2] is the determining factor, and that the addition of hydrochloric acid to the chloroimido ester,



does not necessarily lead to univalent nitrogen by loss of hydrochloric acid since both the hydrogen and the chlorine attached to nitrogen have like sign, viz., (+). Consequently, the loss of chlorine ($Cl^+.Cl^-$) would seem to be the more probable reaction, and is at any rate the one which actually does occur. In the case of chloroamide or bromoamide salts[3] there is a very singular difference in behavior; in the presence of alkali these salts rearrange with great readiness. An inspection of the formulas will show that, similarly, in this case both the halogen and the sodium must be represented with a + charge.



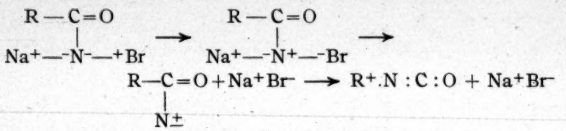
[1] Stieglitz: THIS JOURNAL, **40**, 40 (1908).

[2] Noyes: J. Am. Chem. Soc., **23**, 463 (1901). Stieglitz: *Ibid.*, **23**, 769 (1901); **29**, 51 (1903). Walden: Z. physik. Chem., **43**, 407–43 (1903). J. J. Thompson: The Corpuscular Theory of Matter, p. 130 (1907). Stieglitz and Peterson: Ber. d chem. Ges., **43**, 782 (1910).

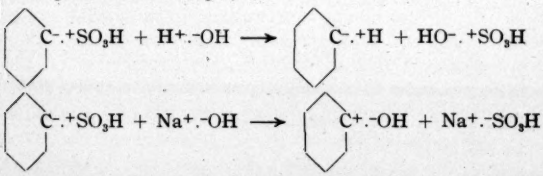
[3] Van Dam: Rec. trav. chim., **18**, 408 (1899).

In terms of the corpuscular atomic hypothesis, before a loss of Na^+Br^- can occur, there must be an interchange of electrons between the nitrogen and the bromine[1] which may be represented as follows:

With this transfer accomplished, which amounts to an intramolecular oxidation, the resulting compound would be a salt of the hydrobromic acid ester of a hydroxamic acid, and the loss of Na^+Br^- would be comparable to the loss of $K^+.^-O.CO.C_6H_5$ from the potassium salt of the benzoyl ester of phenylacethydroxamic acid described above. The complete rearrangement of the bromoamide would be pictured as follows:



Reactions with other classes of organic compounds will be found to require similar assumptions in terms of the corpuscular atomic hypothesis. Thus, benzenesulphonic acid with superheated steam[3] gives benzene and sulphuric acid (comparable to the formation of an amide and hypobromous acid from a bromoamide); but upon fusion with sodium hydroxide it yields phenol and a sulphite.



[1] Stieglitz: THIS JOURNAL, **29**, 51 (1903). Stieglitz and Peterson: Ber. d. chem. Ges., **43**, 782 (1910).

[2] Or,

[3] Some sulphonic acids pass so readily into hydrocarbons that thorough mixing with concentrated sulphuric acid in the cold will bring about this change.

In this case the hypothesis requires a transfer of negative electrons from carbon to sulphur. The difficulty would be the same if the sulphonic acid were regarded as a derivative of sulphurous acid, except that the negative electrons would then pass from sulphur to carbon. In a similar manner, hydroxylaminesulphonic acid, $(HO)HNSO_3H$, or its salts, with water and dilute acids decomposed to give hydroxylamine[1] and sulphuric acid. On the other hand, with sodium hydroxide and water, they probably gave dihydroxylamine, $(HO)_2NH$, which subsequently was converted into a salt of hyponitrous acid.[2]

$$\text{I. } HONHSO_3H + H^+.^-OH \longrightarrow HONH_2 + HO^-.^+SO_3H \longrightarrow NH_3(OH)SO_4.$$

$$\text{II. } 2HONHSO_3H + 6Na^+.^-OH \longrightarrow 2HONHOH + 2Na^+.^-SO_3Na + 2NaOH + 2H_2O \longrightarrow Na_2O_2N_2 + 2Na_2SO_3 + 6H_2O$$

If the Beckmann rearrangement depends solely upon the formation of univalent nitrogen, which in the case of oximes[3] must presume the addition of some reagent, HX, to the double bond, it is not plain at first glance why, upon rearrangement, two oximes of different configurations should not yield the same products, or a mixture of products in the same fixed proportion,[4] a conclusion at variance with our usual experience.[5] For if an oxime should combine with a reagent HX by addition, the double bond would disappear from the formula, and the nitrogen would then be linked by a single bond to carbon, a condition which, in terms of the generally accepted hypothesis, would be expected to lead to free rotation, so that the significance

[1] Raschig: Ber. d. chem. Ges., **20**, 584 (1887). Ann. Chem. (Liebig), **241**, 161 (1887).

[2] Diver and Haga: J. Chem. Soc., **55**, 750 (1889); **75**, 77 (1899). Z. anorg. Chem., **18**, 428 (1898).

[3] Stieglitz: *Loc. cit.*

[4] Montagne: Ber. d. chem. Ges., **43**, 2015 (1910).

[5] Schroeter (Ber. d. chem. Ges., **44**, 1207 (1911)) has recently shown that some doubt may be attached to our methods of determining the configurations of stereoisomeric oximes. When he treated pivalophenone oxime, $(H_3C)_3CC(C_6H_5):NOH$, with phosphorus pentachloride, the tertiary butyl group was found to wander to nitrogen, while with acetic acid and hydrochloric acid the phenyl group was the one which shifted.

of *syn* and *anti* would disappear at once.[1] Schroeter[2] takes exception to this commonly accepted view, and has proposed an hypothesis to avoid it. He assumes that the addition of the reagent HX to the double bond is followed by a subsequent loss of water, hydrogen chloride, etc., to give stereoisomeric univalent nitrogen compounds,

and that the change in position of the groups R and R′ may take place so rapidly that the effect of free rotation, if it occurs at all, may become negligible. This is plainly a case of begging the question, and does not afford an interpretation, but merely a restatement of the difficulty.

Montagne[3] has called attention to the fact that by the addition of some reagent HX to stereoisomeric oximes, intermediate compounds with asymmetric carbon atoms would result, but that this of itself would not account for the differences in the behavior of the two configurations upon rearrangement, since the two optical isomers obtained from one geometrical isomer must be identical with the two optical isomers obtained from the other geometrical isomer.

When these difficulties are looked at seriously, there appear to be peculiar determining factors not yet included in our explanations, the significance of which Stieglitz[4] has not hesitated to acknowledge in the following statement: "The problem of the influence of stereoisomerism must be subjected to critical experimental investigation."

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[1] Montagne: *Loc. cit.*
[2] *Loc. cit.*
[3] Montagne: Ber. d. chem. Ges., **43**, 2015 (1910).
[4] Stieglitz: THIS JOURNAL, **18**, 154 (1896), note.

THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT HIGH TEMPERATURES[1]

By H. N. Morse, W. W. Holland, C. N. Myers, G. Cash and J. B. Zinn

It was shown in our last paper[2] that between 0° and 25° the osmotic pressures of all concentrations of cane sugar solutions, up to that in which a gram-molecular weight of the substance is dissolved in 1000 grams of water, obey quite exactly the law of Gay-Lussac for gases; in other words, that between these limits of temperature the ratio of osmotic to calculated gas pressure is constant for each concentration of solution. On the other hand, it was not obvious from the pressures obtained between 0° and 25° whether they do, or do not, obey the law of Boyle for gases. The osmotic pressures which were measured were all larger than the corresponding calculated gas pressures of the solute; and, in general, they were not proportional to the supposed concentrations of the solutions. The constancy of the osmotic-gas pressure ratio for each concentration, and the variation in the ratios with changes in concentration, are shown in Table I, which is borrowed from the paper to which reference has been made.

It will be seen that the osmotic pressures exceeded the calculated gas pressures by not less than 6 per cent. (0.2, 0.3 and 0.4 weight-normal solutions), and that the excess of the former over the latter increases, with increasing concentration, from the 0.4 normal, until it reaches 11.5 per cent. in the case of the normal solution. It will also be noted that the ratio of osmotic to gas pressure is the same (1.083) in the 0.1 and 0.8 normal solutions. The anomaly presented by the 0.1 normal solution near its freezing point has been referred to in the previous paper.

The fact that, within the field covered by our experiments, which are summarized in the table, the osmotic pressures are

[1] The work upon osmotic pressure, which is in progress in this laboratory, is aided by grants from the Carnegie Institution. Up to the present time 24 papers on the subject have been published. They will be found in This Journal, **28**, 80; **28**, 1; **29**, 137; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425 and 558; **38**, 175; **39**, 667; **40**, 1, 194, 266 and 325; **41**, 1, 92 and 557; **46**, 91, 237, 283, 517 and 554.

[2] This Journal, **45**, 554.

Table I

	Weight-normal concentration									
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	Ratio of osmotic to gas pressure									
Temp.										
0°	(1.106)	1.061	1.061	1.060	1.0685	1.0765	1.083	1.093	1.104	1.115
5°	1.082	1.063	1.058	1.059	1.067	1.074	1.084	1.093	1.102	1.115
10°	1.082	1.060	1.059	1.060	1.066	1.073	1.083	1.092	1.102	1.113
15°	1.082	1.061	1.061	1.059	1.068	1.073	1.083	1.093	1.102	1.115
20°	1.084	1.062	1.060	1.060	1.067	1.073	1.084	1.093	1.103	1.115
25°	1.084	1.059	1.060	1.059	1.065	1.071	1.083	1.093	1.102	1.113
Mean	1.083	1.061	1.060	1.060	1.067	1.074	1.083	1.093	1.103	1.114

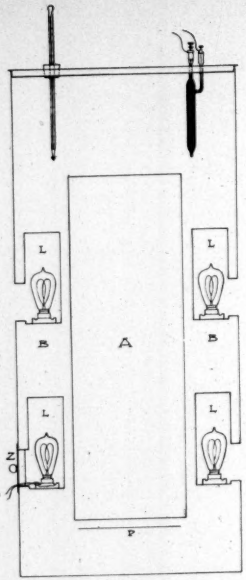

Fig. I

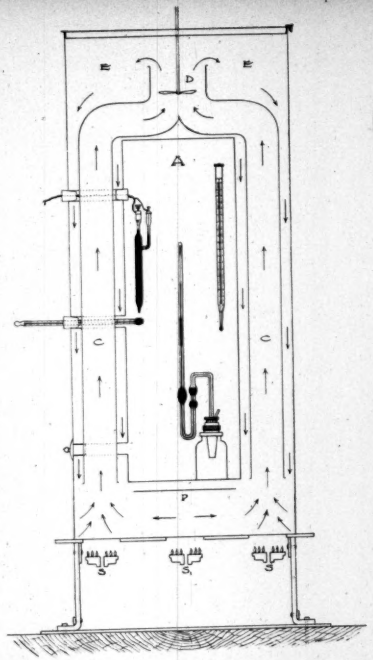

Fig. II

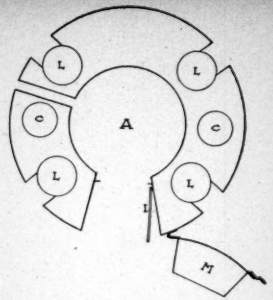

Fig. III

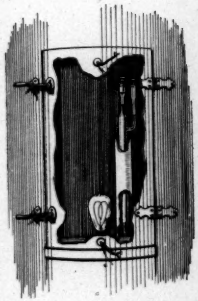

Fig. V

seemingly excessive and not proportional to the supposed concentration of the solutions was not to be accepted as evidence unfavorable to the law of Boyle; for it was conceivable that the apparent anomalies might be due to the unknown molecular relations between the solute and portions of the solvent, which, in effect, cause the solutions to become more concentrated. At all events, it was reasonable to suppose that such relations, if they do exist, would become more simple at higher temperatures. On this account it was deemed important to measure the osmotic pressure of our solutions at temperatures above 25°. This work was already in progress when the last paper was prepared for publication, and we were able to state before closing it "*that the ratios of osmotic to gas pressure, which are so constant for each concentration between 0° and 25°, begin to decline at some temperature between 25° and 30°, and that the rate of decrease is such as to lead one to suspect that the ratios will become unity for all concentrations at temperatures below the boiling point of the solvent.*" In the present paper it will be shown that osmotic and calculated gas pressures become equal in all the concentrations with which we have worked at temperatures not above 80°.

Only one of the baths which were in use when the later work was begun was well adapted to the measurement of osmotic pressure at high temperatures. It was therefore necessary to construct others of a type somewhat different from those described in a recent paper.[1] The new baths are of two sizes, and are made wholly of heavy sheet brass and copper—mainly of the former. *A*, Fig. I, exhibits a section of the inner compartment of one of the smaller baths. It is this compartment which is maintained at any desired constant temperature, and in which the cells are located during a measurement of pressure. It is circular in form in the smaller baths, 300 millimeters in diameter, and one meter in height. Surrounding this is a larger cylinder, *B*,*B*, twice as wide and much higher. In the space between the two brass cylinders the water is heated and made to circulate rapidly over the exterior surface of the inner compartment, *A*. The circulating

[1] THIS JOURNAL, **45**, 383.

system and the arrangements for heating the water by gas are shown in Fig. II. *C,C* are the pumping tubes, 100 millimeters in diameter, which unite at the top in the short but wider tube *D*. At the bottom, they open directly over the gas stoves *S,S*. There is a third gas stove, S_1, which is not ordinarily in use. The water, heated by the stoves *S,S*, is pumped up through the tube *C,C*, at the rate of about 500 liters per minute. At the top of *D* it is delivered into the space *E,E*, and returns to the bottom of the outer cylinder to be reheated and again pumped up through the tubes *C,C*. In its downward course, the water passes over the outer surface of *A*, also over the lamp compartments, *L,L,L,L*. In the smaller baths, there are six of these lamp compartments, and in the larger ones, 8. They are distributed in pairs, one in each pair being located directly over the other. The circular openings to the lamp compartments are closed on the outside by means of caps, one of which, *Z*, is shown in Fig. I. Below the inner bath space *A*, Figs. I and II, is the disk *P*, which has nearly the same diameter as the former. It is so placed in order to prevent water which has been heated by the stove S_1 from rising directly against the bottom of *A*. In Fig. II there are also to be seen three tubes, indicated by dotted lines, which serve as passage ways between the exterior and interior for the introduction of thermometer, wires, etc.

Fig. III is a horizontal section of one of the smaller baths, in which the positions of the pumping tubes are indicated by *C,C*, and those of the lamp compartments by *L,L,L* and *L*. The entrance to the inner bath (150 millimeters in width) is closed by the plate-glass door *I*, and by the hollow metal door *M*. There are two such metal doors, as will be seen in Figs. IV and VI. The lower one, which is opened only when it is necessary to introduce or remove the cells, is packed with hair. The upper door, on the other hand, must be opened whenever an observation is to be made. On this account it is provided with an independent temperature-regulating device, portions of which can be seen in Fig. V. The door is thus prevented from cooling down when open. The space between the inner glass door and the outer metal door is about

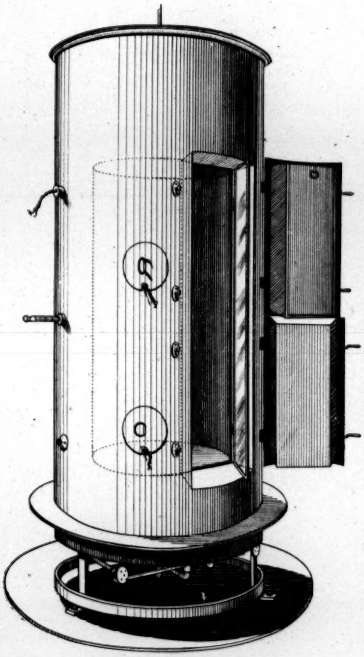

Fig. IV

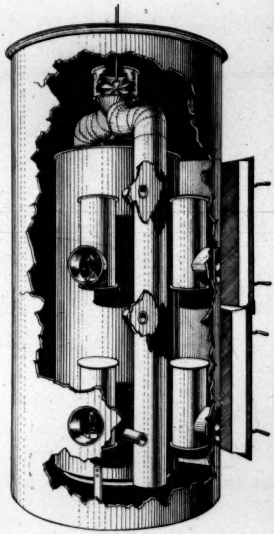

Fig. VI

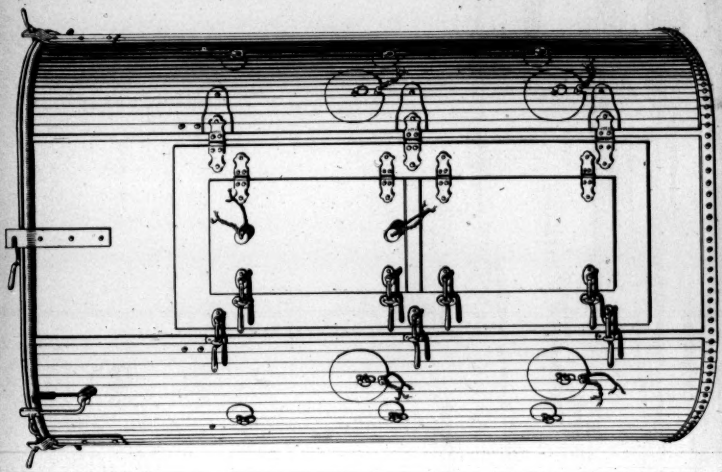

Fig. VIII

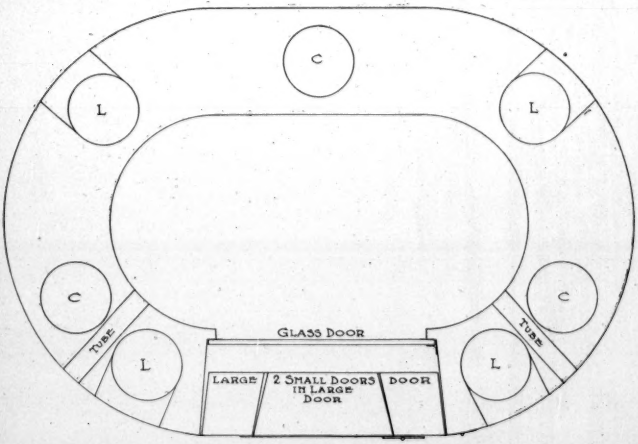

Fig. VII

40 millimeters in width. It is occupied by a brass frame, as large as the glass door, which is filled with minute doors, any one of which can be opened independently of the others. Between this frame, which is placed next to the glass door, and the outer metal doors, is a hair-filled pad, which is so divided that any small portion of the frame may be exposed to view. With these arrangements, it is practicable to read objects in the bath with very slight exposure of the interior. Fig. VI represents the bath with a portion of the exterior removed in order to show the interior relations of the various parts.

Fig. VII is a horizontal section of one of the larger baths which, like those just described, are used for the measurement of osmotic pressure, and also for all the purposes for which the so-called "manometer house"[1] was formerly employed. It is elliptical in form, the longer axis of the interior compartment being twice the diameter of the corresponding part, *A*, in the smaller baths. It has three pumping tubes, *C*,*C* and *C*, instead of two; and 8 lamp compartments, *L*,*L*,*L* and *L*, instead of six. The inner space is ample enough to accommodate the "steel block," the "tappers," and all other appliances which are used in the determination of the capillary depression and the nitrogen volumes of the manometers, and in the comparison of these instruments, one with another. The two smaller metallic doors of the larger bath are like the doors of the smaller bath, except that they are inserted in a larger door which serves them as a frame. The relations of the three doors will be seen in Figs. VII and VIII. The largest door and the lower smaller one are packed with hair, and are opened only when it is necessary to introduce or remove apparatus, or to make some adjustment of the instruments within. The upper smaller door of the larger baths is provided with a device, Fig. V, for the independent regulation of its temperature. It is the only one opened when an observation is to be made. As regards the disposition of the space between the glass and the metal doors, there is no difference between the larger baths and the smaller ones.

Whatever the type of the bath may be which is employed

[1] This Journal, **45**, 337.

in this investigation, the greatest practicable proportion of the heating is effected by means of gas, and only so much of it is left to the electrical devices as is necessary for effective regulation. Hence, in maintaining the baths just described at temperatures as high as 80°, no lamps of over 16 candle-power are employed. At lower temperatures, lamps of 8 or 10 candle-power suffice. If temperatures but little above that of the room are to be maintained, the electrical appliances only are employed to heat and regulate the baths. For low temperatures, a coil of block-tin pipe is placed in the space *E*,*E*, Fig. II; and through it there is made to circulate, under constant pressure, a current of hydrant water, which has been previously cooled, if necessary.

In Fig. II, the thermostat is shown within the compartment *A*, while in Fig. I it is represented as being immersed in the water of the bath. The latter has been found to be the better of the two possible positions for this instrument. The temperature of the water about the thermostat may not be precisely that of the interior compartment, and at other points it may vary slightly; but when the instrument has once been set for a given interior temperature, it is quite capable of maintaining it for any length of time to within 0°.01, which is a rather better regulation than we were able to secure in the older types of baths.

The measurement of osmotic pressure at high temperatures is attended with some difficulties which are not due exclusively to the discomfort of manipulation. Owing to the much lower temperature of the air and of surrounding objects, it is difficult to fill, close and transport the cell to the bath without any appreciable fall in the temperature of the solution. In the same way, the mercury in the manometer cools down during the operations connected with the "setting up" of the cell. When, later, the temperature of the two liquids—the solution and the mercury—has again risen to that of the bath, the compression of the nitrogen, due to their expansion, may exceed the osmotic pressure. If it does, some *concentration* of the solution must ensue. When the over-compression of the nitrogen is minute in comparison with the volume of the

solution, the resulting concentration cannot be detected by the polariscope and is, of course, negligible. But the proportion of the experiments in which concentration *can* be detected by the polariscope increases as the work is carried out at the higher temperatures. At moderate temperatures it is rarely detectable.

It is customary, in preparing a cell for the bath, to bring upon the enclosed solution an initial pressure which, together with any additional pressure due to an expected expansion of the liquids, is intended to nearly equal the osmotic pressure. At high temperatures, the allowance made for such expansion is usually insufficient; hence a majority of the cells, after coming to the temperature in the bath, begin their records with pressures which exceed the osmotic pressures of the solutions. As we have shown elsewhere, experiments in which concentration has occurred need not be rejected, provided the exact amount of the concentration can be determined, as it can be, in the case of cane sugar, by means of the polariscope. Nevertheless, we have excluded from the records which follow every experiment, except one, in which concentration could be discovered. In other words, all the solutions of which the records are presented exhibited the same rotations, when removed from the cells, as did other portions of the corresponding original solutions which were reserved for comparison. The exception referred to (Table VIII) is introduced merely to illustrate what may occur when a cell begins its record with a too large over-pressure. The proportion of the whole number of experiments which was excluded in accordance with our rule was less than 10 per cent.

At temperatures above 40°, all glass apparatus which was used in the baths became quite brittle. It was necessary, on this account, to replace the bottles in which the cells are immersed in water during an experiment, and the glasses used in depositing the membranes, with vessels made of copper. The most serious result of the effect of temperature upon the character of the glass was experienced in connection with the manometers. The calibrated portion of these instruments, together with the various bulbs, is detached from the end carry-

ing the "cone" whenever any manipulation of the latter is necessary which might endanger the really valuable part of the manometer. Afterwards, the detached portion is again fused onto the tube which passes through the cone. Owing to the necessity of renewing the rubber on the cone after each experiment, and of frequently "resetting" the tube in the cone with fusible metal, the operation is a constantly recurring one. At moderate temperatures, it gives no trouble, but above 40° the glass of the manometer becomes so brittle that it is necessary carefully to "anneal" the instrument before the operation can be carried out successfully.

In the work between 0° and 25°, the osmotic pressure of the usual 10 concentrations of solution was determined at intervals of 5 degrees, namely, at 0°, 5°, 10°, 15°, 20° and 25°. In the present investigation, the intervals of temperature, after passing 30°, have been doubled. The work at 30°, 40°, 50° and 60° is finished, while that at 70° and 80° is still incomplete. The first question to be answered was: "*At what temperature does the osmotic pressure of each of the 10 concentrations become equal to the calculated gas pressure of the solute?*" That question has been answered definitely, and to this extent the investigation is complete and ready for publicity. There remains to be answered a second question, namely, *whether, when at some temperature the osmotic and calculated gas pressures have become equal, the same relation is maintained at still higher temperatures.* The data which follow furnish only a partial answer to the second question.

The membranes in some of the cells employed in the present investigation had been in use for more than two years, and had acquired in a marked degree the characteristics of *maturity*. These are (1) *reliability*, in the sense that they never give way and become leaky under pressure; and (2) *slowness*, in the sense that the water which must be added to or rather abstracted from the solutions in order to establish equilibrium, requires much time for its passage through the membrane material. They respond very slowly to fluctuations in the volume of the solutions and to changes in atmospheric pressure; in short, they are especially subject to "*ther-*

mometer" and "*barometer effects.*" The remedy is to allow cells containing "*mature*" membranes to make long records in the bath, and to correct the mean total pressure of the several days for the mean barometer of the same period. The records will show that the remedy has been applied. The cells have been allowed to remain in the baths much longer than is necessary when the membranes are comparatively fresh; and the *mean* barometer correction has been applied in all cases.

Wherever the cell has required five days or more in order to establish the final equilibrium—within the range of *thermometer* and *barometer effects*—a "preliminary record" for the period has been given. The preliminary record is, however, not always strictly reliable; for during the preliminary period we sometimes test the cell by attempting to turn up the tightening collar, and this treatment is usually followed by a slight increase in the pressure. Such manipulation is never resorted to after the cell has begun its "final" record.

Table II

0.1 Wt. normal solution. Expt. 1 at 30°. Cell Ni_2. Resistance of membrane (nickel ferrocyanide), 500,000 ohms. Manometer 1. Calc. gas pressure, 2.472 atms. Time of setting up cell, April 6, 1911. Barometer during final record: max., 1.010; min., 0.990. Total pressures (daily):

Preliminary Record

	Atms.		Atms.		Atms.
April 8,	3.713	April 13,	3.637	April 17,	3.528
9,	3.711	14,	3.580	18,	3.526
10,	3.702	15,	3.557	19,	3.492
11,	3.687	16,	3.525	20,	3.493
12,	3.660				

(13 days)

Final Record

	Atms.		Atms.		Atms.
April 21,	3.482	April 25,	3.477	April 28,	3.484
22,	3.465	26,	3.481	29,	3.467
23,	3.492	27,	3.482	30,	3.463
24,	3.488				

(10 days)

Mean total pressure, April 21–30 = 3.4781 atms.
Mean barom. pressure, April 21–30 = 1.0025 atms.
Mean osmot. pressure, April 21–30 = 2.4756 atms.

Table III

0.1 Wt. normal solution. Expt. 2 at 30°. Cell K_3. Resistance, 250,000 ohms. Manometer 15. Calc. gas pressure, 2.472 atms. Time of setting up cell, November 13, 1911. Barometer during final record: max., 1.009; min., 0.982. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 14,	3.482	Nov. 18,	3.462	Nov. 22,	3.474
15,	3.468	17,	3.466	23,	3.475
16,	3.463	20,	3.462	24,	3.475
17,	3.465	21,	3.466	(11 days)	

Mean total pressure, Nov. 14–24 = 3.4681 atms.
Mean barom. pressure, Nov. 14–24 = 0.996 atms.
Mean osmot. pressure, Nov. 14–24 = 2.4721 atms.

Table IV

0.1 Wt. normal solution. Expt. 3 at 30°. Cell F_3. Resistance, 209,000 ohms. Manometer 24. Calc. gas pressure, 2.472 atms. Time of setting up cell, November 24, 1911. Barometer during final record: max., 1.013; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 27,	3.468	Dec. 1,	3.464	Dec. 4,	3.476
28,	3.461	2,	3.469	5,	3.480
29,	3.458	3,	3.472	6,	3.483
30,	3.461			(10 days)	

Mean total pressure, Nov. 27–Dec. 6 = 3.4692 atms.
Mean barom. pressure, Nov. 27–Dec. 6 = 1.001 atms.
Mean osmot. pressure, Nov. 27–Dec. 6 = 2.4682 atms.

Table V

0.1 Wt. normal solution. Expt. 4 at 30°. Cell L_8. Resistance, 159,000 ohms. Manometer 15. Calc. gas pressure, 2.472 atms. Time of setting up cell, November 24, 1911. Barometer during final record: max., 1.013; min., 0.996. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 25,	3.461	Nov. 29,	3.484	Dec. 3,	3.481
26,	3.465	30,	3.489	4,	3.484
27,	3.479	Dec. 1,	3.492	5,	3.485
28,	3.484	2,	3.484	6,	3.491
				(12 days)	

Mean total pressure, Nov. 25–Dec. 6 = 3.4816 atms.
Mean barom. pressure, Nov. 25–Dec. 6 = 1.002 atms.
Mean osmot. pressure, Nov. 25–Dec. 6 = 2.4796 atms.
Mean osmotic pressure for Expts. 1, 2, 3 and 4 = 2.474 atms.
Ratio of osmotic to calc. gas pressure = 1.000

Table VI

0.1 Wt. normal solution. Expt. 1 at 40°. Cell E_3. Resistance, 600,000 ohms. Manometer 9. Calc. gas pressure, 2.553 atms. Time of setting up cell, April 3, 1911. Barometer during final record: max., 1.017; min., 0.994. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
April 4,	3.709	April 6,	3.680	April 8,	(not recorded)
5,	3.701	7,	(not recorded)		(5 days)

Final Record

	Atms.		Atms.		Atms.
April 9,	3.563	April 13,	3.567	April 16,	3.553
10,	3.568	14,	3.564	17,	3.552
11,	3.567	15,	3.559	18,	3.546
12,	3.567				(10 days)

Mean total pressure, Apr. 9–18 = 3.5606 atms.
Mean barom. pressure, Apr. 9–18 = 1.006 atms.
Mean osmot. pressure, Apr. 9–18 = 2.5546 atms.

Table VII

0.1 Wt. normal solution. Expt. 2 at 40°. Sell F_3. Resistance, 95,000 ohms. Manometer 24. Calc. gas pressure, 2.553 atms. Time of setting up cell, April 3, 1911. Barometer during final record: max., 1.017; min., 0.994. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 4,	4.473	Apr. 6,	3.849	Apr. 3,	3.615
5,	4.048	7,	3.687		(5 days)

Final Record

	Atms.		Atms.		Atms.
Apr. 9,	3.563	Apr. 13,	3.588	Apr. 17,	3.552
10,	3.578	14,	3.575	18,	3.546
11,	3.577	15,	3.571		(10 days)
12,	3.581	16,	3.565		

Mean total pressure, Apr. 9–18 = 3.5696 atms.
Mean barom. pressure, Apr. 9–18 = 1.008 atms.
Mean osmot. pressure, Apr. 9–18 = 2.5616 atms.

Table VIII.—(Example of Concentration in the Cell)

0.1 Wt. normal solution. Expt. 3 at 40°. Cell D_5. Resistance of membrane, 120,000 ohms. Manometer 22. Calc. gas pressure, 2.553 atms. Time of setting up cell, April 3, 1911. Barometer during final record: max., 1.017; min., 0.995. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 4,	4.065	Apr. 6,	3.770	Apr. 8,	3.670
5,	3.815	7,	3.698		(5 days)

Final Record

	Atms.		Atms.		Atms.
Apr. 9,	3.663	Apr. 12,	3.661	Apr. 15,	3.646
10,	3.657	13,	3.656	16,	3.644
11,	3.657	14,	3.546	17,	3.637

Mean total pressure, Apr. 9–17 = 3.652 atms.
Mean barom. pressure, Apr. 9–17 = 1.008 atms.
Mean osmot. pressure, Apr. 9–17 = 2.644 atms.

Gain in rotation = 0°.45 = 0.081 atm. Corrected osmotic pressure = 2.563 atms. Mean osmotic pressure for Experiments 1, 2 and 3 = 2.5597 atms. Ratio of osmotic to gas pressure = 1.003.

Table IX

0.1 Wt. normal solution. Expt. 1 at 50°. Cell U_5. Resistance, 55,000 ohms. Manometer 1. Calc. gas pressure, 2.635 atms. Time of setting up cell, Dec. 7, 1911. Barometer during final record: max., 1.014; min., 0.981. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 8,	3.927	Dec. 11,	3.775	Dec. 14,	3.729
9,	3.831	12,	3.774	15,	3.718
10,	3.791	13,	3.728	16,	3.686

Final Record

	Atms.		Atms.		Atms.
Dec. 17,	3.650	Dec. 21,	3.649	Dec. 25,	3.650
18,	3.646	22,	3.644	26,	3.644
19,	3.643	23,	3.646	27,	3.643
20,	3.648	24,	3.650	28,	3.644

Mean total pressure, Dec. 17–28 = 3.646 atms.
Mean barom. pressure, Dec. 17–28 = 1.003 atms.
Mean osmot. pressure, Dec. 17–28 = 2.643 atms.

Table X

0.1 Wt. normal solution. Expt. 2 at 50°. Cell E_3. Resistance, 100,000 ohms. Manometer 15. Calc. gas pressure, 2.635 atms. Time of setting up cell, Dec. 8, 1911. Barometer during final record: max., 1.014; min., 0.989. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 9,	4.766	Dec. 12,	3.766	Dec. 15,	3.671
10,	4.523	13,	3.744	16,	3.666
11,	4.380	14,	3.713		(8 days)

Final Record

	Atms.		Atms.		Atms.
Dec. 17,	3.644	Dec. 21,	3.642	Dec. 24,	3.635
18,	3.637	22,	3.637	25,	3.635
19,	3.642	23,	3.635	26,	3.635
20,	3.646				(10 days)

Mean total pressure, Dec. 17–26 = 3.6388 atms.
Mean barom. pressure, Dec. 17–26 = 1.005 atms.
Mean osmot. pressure, Dec. 17–27 = 2.6338 atms.

Table XI

0.1 Wt. normal solution. Expt. 3 at 50°. Cell V_3. Resistance, 110,000 ohms. Manometer 9. Calc. gas pressure, 2.635 atms. Time of setting up cell, Dec. 12, 1911. Barometer during final record: max., 1.014; min., 0.981. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 13,	4.203	Dec. 15,	3.419	Dec. 17,	3.654
14,	3.417	16,	3.712[1]		

Final Record

	Atms.		Atms.		Atms.
Dec. 18,	3.632	Dec. 22,	3.629	Dec. 26,	3.630
19,	3.627	23,	3.629	27,	3.624
20,	(not rec'd)	24,	3.629	28,	3.629
21,	(not rec'd)	25,	3.630		(11 days)

Mean total pressure, Dec. 18–28 = 3.629 atms.
Mean. barom. pressure, Dec. 18–28 = 1.000 atm.
Mean osmot. pressure, Dec. 18–28 = 2.629 atms.
Mean osmotic pressure of Expts. 1, 2 and 3 = 2.6353 atms.
Ratio of osmotic to gas pressure = 1.000

[1] Manometer tightened.

Table XII

0.1 Wt. normal solution. Expt. 1 at 60°. Cell W_5. Resistance, 37,000 ohms. Manometer 15. Calc. gas pressure, 2.717 atms. Time of setting up cell, Feb. 15, 1912. Barometer during final record: max., 1.018; min., 0.983. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 16,	4.897	Feb. 19,	4.189	Feb. 22,	3.866
17,	4.622	20,	4.325	23,	3.788
18,	4.408	21,	3.927	24,	3.770

Final Record

	Atms.		Atms.		Atms.
Feb. 25,	3.724	Feb. 29,	3.720	Mar. 3,	3.732
26,	3.721	Mar. 1,	3.729	4,	3.730
27,	3.720	2,	3.731	5,	3.731
28,	3.714				

Mean total pressure, Feb. 25–Mar. 5 = 3.7252 atms.
Mean barom. pressure, Feb. 25–Mar. 5 = 1.005 atms.
Mean osmot. pressure, Feb. 25–Mar. 5 = 2.7202 atms.

Table XIII

0.1 Wt. normal solution. Expt. 2 at 60°. Cell B_5. Resistance, 37,000 ohms. Manometer 11. Calc. gas pressure, 2.717 atms. Time of setting up cell, Feb. 15, 1912. Barometer during final record: max., 1.018; min., 0.983. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 16,	4.520	Feb. 19,	4.122	Feb. 22,	3.898
17,	4.346	20,	4.002	23,	3.780
18,	4.310	21,	3.960	24,	3.787

Final Record

	Atms.		Atms.		Atms.
Feb. 25,	3.718	Feb. 29,	3.713	Mar. 4,	3.726
26,	3.719	Mar. 1,	3.718	5,	3.726
27,	3.716	2,	3.722		(10 days)
28,	3.708	3,	3.726		

Mean total pressure, Feb. 25–Mar. 5 = 3.7192 atms.
Mean barom. pressure, Feb. 25–Mar. 5 = 1.005 atms.
Mean osmot. pressure, Feb. 25–Mar. 5 = 2.7142 atms.
Mean osmotic pressure of Expts. 1 and 2 = 2.7172 atms.
Ratio of osmotic to gas pressure = 1.000

Table XIV

0.2 Wt. normal solution. Expt. 1 at 30°. Cell C_3. Resistance, 120,000 ohms. Manometer 9. Calc. gas pressure, 4.943 atms. Time of setting up cell, October 30, 1911. Barometer during final record: max., 1.018; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 2,	6.049	Nov. 6,	6.045	Nov. 9,	6.046
3,	6.031	7,	6.045	10,	6.046
4,	6.039	8,	6.044	11,	6.046
5,	6.046				(10 days)

Mean total pressure, Nov. 2–11 = 6.0437 atms.
Mean barom. pressure, Nov. 2–11 = 1.004 atms.
Mean osmot. pressure, Nov. 2–11 = 5.0397 atms.

Table XV

0.2 Wt. normal solution. Expt. 2 at 30°. Cell L_8. Resistance, 150,000 ohms. Manometer 20. Calc. gas pressure, 4.943 atms. Time of setting up cell, October 30, 1911. Barometer during final record: max., 1.018; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 3,	6.056	Nov. 7,	6.042	Nov. 11,	6.041
4,	6.052	8,	6.040	12,	6.039
5,	6.050	9,	6.038	13,	6.053
6,	6.046	10,	6.041		(11 days)

Mean total pressure, Nov. 3–13 = 6.0498 atms.
Mean barom. pressure, Nov. 3–13 = 1.002 atms.
Mean osmot. pressure, Nov. 3–13 = 5.0478 atms.
Mean osmotic pressure for Expts. 1 and 2 = 5.0438 atms.
Ratio of osmotic to gas pressure = 1.020

Table XVI

0.2 Wt. normal solution. Expt. 1 at 40°. Cell I_3. Resistance, 120,000 ohms. Manometer 11. Calc. gas pressure, 5.106 atms. Time of setting up cell, March 22, 1911. Barometer during final record: max., 1.016; min., 0.974. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 24,	6.176	Mar. 27,	(not rec'd)	Mar. 30,	6.150
25,	6.159	28,	6.169	31,	6.147
26,	6.179	29,	(not rec'd)	Apr. 1,	6.166

Mean total pressure, Mar. 24–Apr. 1 = 6.164 atms.
Mean barom. pressure, Mar. 24–Apr. 1 = 0.996 atms.
Mean osmot. pressure, Mar. 24–Apr. 1 = 5.168 atms.

Table XVII

0.2 Wt. normal solution. Expt. 2 at 40°. Cell P_3. Resistance, 150,000 ohms. Manometer 5. Calc. gas pressure, 5.106 atms. Time of setting up cell, March 22, 1911. Barometer during final record: max., 1.016; min., 0.997. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 24,	6.715	Mar. 29,	6.307	Apr. 3,	(not rec'd)
25,	6.600	30,	6.236	4,	6.193
26,	6.505	31,	6.228	5,	6.204
27,	6.412	Apr. 1,	6.268	6,	6.192
28,	6.319	2,	6.282	7,	6.178

Final Record

	Atms.		Atms.		Atms.
Apr. 8,	6.162	Apr. 10,	6.180	Apr. 12,	6.166
9,	6.162	11,	6.176	13,	6.165

Mean total pressure, April 8–13 = 6.1685 atms.
Mean barom. pressure, April 8–13 = 1.0105 atms.
Mean osmot. pressure, April 8–13 = 5.158 atms.
Mean osmotic pressure of Expts. 1 and 2 = 5.163 atms.
Ratio of osmotic to gas pressure = 1.011

Table XVIII

0.2 Wt. normal solution. Expt. 1 at 50°. Cell L_5. Resistance, 75,000 ohms. Manometer 29. Calc. gas pressure, 5.27 atms. Time of setting up cell, November 28, 1911. Barometer during final record: max., 1.011; min., 0.997. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Nov. 29,	7.552	Dec. 1,	6.518	Dec. 3,	6.186
30,	(not rec'd)	2,	6.165		

Final Record

	Atms.		Atms.		Atms.
Dec. 4,	6.281	Dec. 8,	6.284	Dec. 11,	6.285
5,	6.263	9,	6.285	12,	6.288
6,	6.277	10,	6.283	13,	6.287
7,	6.280				(10 days)

Mean total pressure, Dec. 4–13 = 6.2813 atms.
Mean barom. pressure, Dec. 4–13 = 1.008 atms.
Mean osmot. pressure, Dec. 4–13 = 5.2733 atms.

Table XIX

0.2 Wt. normal solution. Expt. 2 at 50°. Cell S_3. Resistance, 65,000 ohms. Manometer 39. Calc. gas pressure, 5.27 atms. Time of setting up cell, November 28, 1911. Barometer during final record: max., 1.011; min., 0.997. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Nov. 29,	6.221	Dec. 1,	6.181	Dec. 3,	6.058
30,	(not rec'd)	2,	6.231	4,	6.244

Final Record

	Atms.		Atms.		Atms.
Dec. 5,	6.266	Dec. 9,	6.300	Dec. 12,	6.301
6,	6.290	10,	6.300	13,	6.299
7,	6.300	11,	6.300	14,	6.295
8,	6.299				(10 days)

Mean total pressure, Dec. 5–14 = 6.295 atms.
Mean barom. pressure, Dec. 5–14 = 1.009 atms.
Mean osmot. pressure, Dec. 5–14 = 5.285 atms.

Table XX

0.2 Wt. normal solution. Expt. 3 at 50°. Cell R_5. Resistance, 80,000 ohms. Manometer 27. Calc. gas pressure, 5.27 atms. Time of setting up cell, November 28, 1911. Barometer during final record: max., 1.001; min., 0.997. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Dec. 3,	6.274	Dec. 7,	6.277	Dec. 11,	6.283
4,	6.316	8,	6.279	12,	6.279
5,	6.284	9,	6.282	13,	6.282
6,	6.284	10,	6.279		(11 days)

Mean total pressure, Dec. 3–13 = 6.284 atms.
Mean barom. pressure, Dec. 3–13 = 1.007 atms.
Mean osmot. pressure, Dec. 3–13 = 5.277 atms.
Mean osmotic pressure of Expts. 1, 2 and 3 = 5.2784 atms.
Ratio of osmotic to gas pressure = 1.0016

Table XXI

0.2 Wt. normal solution. Expt. 1 at 60°. Cell E_8. Resistance, 50,000 ohms. Manometer 1. Calc. gas pressure, 5.433 atms. Time of setting up cell, February 7, 1911. Barometer during final record: max., 1.013; min., 0.982. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 8,	6.563	Feb. 10,	6.527	Feb. 12,	6.496
9,	6.549	11,	6.510		

Final Record

	Atms.		Atms.		Atms.
Feb. 13,	6.457	Feb. 17,	6.452	Feb. 21,	6.414
14,	6.449	18,	6.445	22,	6.417
15,	6.441	19,	6.444	23,	6.436
16,	6.456	20,	6.449		(11 days)

Mean total pressure, Feb. 13–23 = 6.446 atms.
Mean barom. pressure, Feb. 13–23 = 0.996 atms.
Mean osmot. pressure, Feb. 13–23 = 5.450 atms.

Table XXII

0.2 Wt. normal solution. Expt. 2 at 60°. Cell K_3. Resistance, 61,000 ohms. Manometer 1. Calc. gas pressure, 5.433 atms. Time of setting up cell, February 26, 1911. Barometer during final record: max., 1.013; min., 0.987. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 27,	9.239	Mar. 1,	7.784	Mar. 4,	6.652
28,	8.395	2,	7.222	5,	6.481
29,	8.117	3,	6.930		

Final Record

	Atms.		Atms.		Atms.
Mar. 6,	6.442	Mar. 9,	4.429	Mar. 12,	432.0
7,	6.420	10,	4.430	13,	411.0
9,	6.423	11,	4.427	14,	416.0

Mean total pressure, Mar. 6–14 = 6.4256 atms.
Mean barom. pressure, Mar. 6–14 = 1.001 atms.
Mean osmot. pressure, Mar. 6–14 = 5.4246 atms.
Mean osmotic pressure of Expts. 1 and 2 = 5.4373 atms.
Ratio of osmotic to gas pressure = 1.0008

Table XXIII

0.3 Wt. normal solution. Expt. 1 at 30°. Cell B_3. Resistance, 110,000 ohms. Manometer 11. Calc. gas pressure, 7.415 atms. Time of setting up cell, October 25, 1911. Barometer during final record: max., 1.018; min., 0.989. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Oct. 27,	10.185	Oct. 29,	8.845	Oct. 31,	8.703
28,	8.945	30,	8.765	Nov. 1,	8.662

Final Record

	Atms.		Atms.		Atms.
Nov. 2,	8.660	Nov. 6,	8.646	Nov. 9,	8.641
3,	8.654	7,	8.638	10,	8.644
4,	8.640	8,	8.637	11,	8.643
5,	8.646				

Mean total pressure, Nov. 2–11 = 8.6449 atms.
Mean barom. pressure, Nov. 2–11 = 1.004 atms.
Mean osmot. pressure, Nov. 2–11 = 7.6409 atms.

Table XXIV

0.3 Wt. normal solution. Expt. 2 at 30°. Cell H_3. Resistance, 110,000 ohms. Manometer 24. Calc. gas pressure, 7.415 atms. Time of setting up cell, October 25, 1911. Barometer during final record: max., 1.018; min., 0.989. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Oct. 27,	8.710	Oct. 30,	8.561	Nov. 1,	8.900
28,	8.594	31,	8.878	2,	8.746
29,	8.573				(7 days)

Final Record

	Atms.		Atms.		Atms.
Nov. 3,	8.685	Nov. 6,	8.668	Nov. 9,	8.652
4.	8.675	7,	8.648	10,	8.652
5,	8.675	8,	8.650	11,	8.651

Mean total pressure, Nov. 3–11 = 8.6556 atms.
Mean barom. pressure, Nov. 3–11 = 1.003 atms.
Mean osmot. pressure, Nov. 3–11 = 7.6526 atms.
Mean of osmotic pressures of Expts. 1 and 2 = 7.6468 atms.
Ratio of osmotic to gas pressure = 1.031

Table XXV

0.3 Wt. normal solution. Expt. 1 at 40°. Cell D_3. Resistance, 80,000 ohms. Manometer 39. Calc. gas pressure, 7.66 atms. Time of setting up cell, April 21, 1911. Barometer during final record: max., 1.009; min., 0.987. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 22,	7.442	Apr. 25,	8.714	Apr. 27,	8.785
23,	8.532	26,	8.747	28,	8.785
24,	8.571				

Final Record

	Atms.		Atms.		Atms.
Apr. 29,	8.805	May 2,	8.795	May 4,	8.814
30,	8.820	3,	8.807	5,	8.817
May 1,	8.834				

Mean total pressure, Apr. 29–May 5 = 8.813 atms.
Mean barom. pressure, Apr. 29–May 5 = 0.997 atm.
Mean osmot. pressure, Apr. 29–May 5 = 7.817 atms.

Table XXVI

0.3 Wt. normal solution. Expt. 2 at 40°. Cell D_5. Resistance, 110,000 ohms. Manometer 22. Calc. gas pressure, 7.66 atms. Time of setting up cell, April 26, 1911. Barometer: max., 1.010; min., 0.985. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 28,	8.849	May 2,	8.854	May 6,	8.865
29,	8.838	3,	8.856	7,	8.874
30,	8.821	4,	8.865	8,	8.859
May 1,	8.849	5,	8.867		

Mean total pressure, Apr. 28–May 8 = 8.854 atms.
Mean barom. pressure, Apr. 28–May 8 = 1.001 atms.
Mean osmot. pressure, Apr. 28–May 8 = 7.853 atms.

Table XXVII

0.3 Wt. normal solutions. Expt. 3 at 40°. Cell E_5. Resistance, 80,000 ohms. Manometer 6. Calc. gas pressure, 7.66 atms. Time of setting up cell, April 26, 1911. Barometer during final record: max., 1.010; min., 0.993. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 27,	7.736	Apr. 29,	8.717	May 1,	8.799
28,	8.457	30,	8.717		

Final Record

	Atms.		Atms.		Atms.
May 2,	8.854	May 5,	8.839	May 7,	8.820
3,	8.828	6,	8.843	8,	8.813
4,	8.844				

Mean total pressure, May 2–8 = 8.834 atms.
Mean barom. pressure, May 2–8 = 1.003 atms.
Mean osmot. pressure, May 2–8 = 7.831 atms.

Table XXVIII

0.3 Wt. normal solution. Expt. 4 at 40°. Cell F_5. Resistance, 110,000 ohms. Manometer 24. Calc. gas pressure, 7.66 atms. Time of setting up cell, April 26, 1911. Barometer: max., 1.010; min., 0.983. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 29,	8.824	May 3,	8.827	May 6,	8.853
30,	(not rec'd)	4,	8.840	7,	8.848
May 1,	(not rec'd)	5,	8.842	8,	8.846
2,	8.808				

Mean total pressure, Apr. 29–May 8 = 8.836 atms.
Mean barom. pressure, Apr. 29–May 8 = 1.001 atms.
Mean osmot. pressure, Apr. 29–May 8 = 7.835 atms.
Mean osmotic pressure of Expts. 1, 2, 3 and 4 = 7.844 atms.
Ratio of osmotic to gas pressure = 1.024

Table XXIX

0.3 Wt. normal solution. Expt. 1 at 50°. Cell B_3. Resistance 75,000 ohms. Manometer 38. Calc. gas pressure, 7.905 atms. Time of setting up cell, December 6, 1911. Barometer during final record: max., 1.013; min., 0.981. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 7,	10.790	Dec. 12,	9.494	Dec. 16,	9.091
8,	10.498	13,	9.336	17,	9.093
9,	10.158	14,	9.249	18,	8.914
10,	9.805	15,	9.091	19,	8.892
11,	9.647				(13 days)

Final Record

	Atms.		Atms.		Atms.
Dec. 20,	8.945	Dec. 23,	8.968	Dec. 26,	8.968
21,	8.950	24,	8.968	27,	8.961
22,	8.962	25,	8.967	28,	8.964

Mean total pressure, Dec. 20–28 = 8.961 atms.
Mean barom. pressure, Dec. 20–28 = 1.001 atms.
Mean osmot. pressure, Dec. 20–28 = 7.960 atms.

Table XXX

0.3 Wt. normal solution. Expt. 2 at 50°. Cell T_3. Resistance, 60,000 ohms. Manometer 5. Calc. gas pressure, 7.905 atms. Time of setting up cell, December 6, 1911. Barometer during final record: max., 1.014; min., 0.991. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 7,	11.358	Dec. 10,	9.131	Dec. 12,	9.050
8,	10.076	11,	9.106	13,	8.934
9,	9.444				

Final Record

	Atms.		Atms.		Atms.
Dec. 14,	9.005	Dec. 18,	8.978	Dec. 21,	9.003
15,	8.995	19,	8.994	22,	8.995
16,	8.976	20,	9.012	23,	8.991
17,	8.980				(10 days)

Mean total pressure, Dec. 14–23 = 8.9929 atms.
Mean barom. pressure, Dec. 14–23 = 1.005 atms.
Mean osmot. pressure, Dec. 14–23 = 7.9879 atms.

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Table XXXI

0.3 Wt. normal solution. Expt. 3 at 50°. Cell P_3. Resistance, 75,000 ohms. Manometer 2. Calc. gas pressure, 7.905 atms. Time of setting up cell, December 19, 1911. Barometer during final record: max., 1.009; min., 0.981. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Dec. 22,	8.970	Dec. 26,	8.978	Dec. 29,	8.942
23,	8.981	27,	9.001	30,	8.981
24,	8.978	28,	8.959	31,	8.925
25	8.992				(10 days)

Mean total pressure, Dec. 22–31 = 8.9707 atms.
Mean barom. pressure, Dec. 22–31 = 0.997 atm.
Mean osmot. pressure, Dec. 22–31 = 7.9737 atms.
Mean osmotic pressure of Expts. 1, 2 and 3 = 7.9739 atms.
Ratio of osmotic to gas pressure = 1.0087

Table XXXII

0.3 Wt. normal solution. Expt. 1 at 60°. Cell K_3. Resistance, 75,000 ohms. Manometer 15. Calc. gas pressure, 8.150 atms. Time of setting up cell, January 25, 1912. Barometer during final record: max., 1.013; min., 0.995. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 26,	17.252	Jan. 30,	10.314	Feb. 3,	9.253
27,	14.022	31,	9.792	4,	9.210
28,	11.705	Feb. 1,	9.475	5,	9.178
29,	10.960	2,	9.332		(11 days)

Final Record

	Atms.		Atms.		Atms.
Feb. 6,	9.147	Feb. 10,	9.142	Feb. 13,	9.157
7,	9.137	11,	9.151	14,	9.160
8,	9.155	12,	9.161	15,	9.156
9,	9.156				(10 days)

Mean total pressure, Feb. 6–15 = 9.1522 atms.
Mean barom. pressure, Feb. 6–15 = 1.000 atm.
Mean osmot. pressure, Feb. 6–15 = 8.1522 atms.

Table XXXIII

0.3 Wt. normal solutions. Expt. 2 at 60°. Cell F_8. Resistance, 75,000 ohms. Manometer 11. Calc. gas pressure, 8.150 atms. Time of setting up cell, January 25, 1912. Barometer during final record: max., 1.013; min., 0.995. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 26,	9.730	Jan. 30,	9.004	Feb. 3,	9.727
27,	9.274	31,	8.800	4,	9.443
28,	8.837	Feb. 1,	(not rec'd)	5,	9.269
29,	9.025	2,	(not rec'd)		(11 days)

Final Record

	Atms.		Atms.		Atms.
Feb. 6,	9.133	Feb. 10,	9.130	Feb. 13,	9.123
7,	9.153	11,	9.117	14,	9.134
8,	9.136	12,	9.114	15,	9.134
9,	9.109				(10 days)

Mean total pressure, Feb. 6–15 = 9.1283 atms.
Mean barom. pressure, Feb. 6–15 = 1.000 atm.
Mean osmot. pressure, Feb. 6–15 = 8.1283 atms.
Mean osmotic pressure for Expts. 1 and 2 = 8.1403 atms.
Ratio of osmotic to gas pressure = 0.999

Table XXXIV

0.4 Wt. normal solution. Expt. 1 at 30°. Cell L_9. Resistance, 110,000 ohms. Manometer 29. Calc. gas pressure, 9.886 atms. Time of setting up cell, October 13, 1911. Barometer during final record: max., 1.014; min., 0.995. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Oct. 14,	12.080	Oct. 16,	11.556	Oct. 18,	11.375
15,	11.518	17,	11.452	19,	11.331

Final Record

	Atms.		Atms.		Atms.
Oct. 20,	11.309	Oct. 22,	11.305	Oct. 24,	11.294
21,	11.313	23,	11.305	25,	11.313

Mean total pressure, Oct. 20–25 = 11.307 atms.
Mean barom. pressure, Oct. 20–25 = 1.002 atms.
Mean osmot. pressure, Oct. 20–25 = 10.305 atms.

Table XXXV

0.4 Wt. normal solution. Expt. 2 at 30°. Cell C_3. Resistance, 250,000 ohms. Manometer 24. Calc. gas pressure, 9.886 atms. Time of setting up cell, October 13, 1911. Barometer during final record: max., 1.014; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 16,	11.297	Oct. 20,	11.286	Oct. 23,	11.284
17,	11.278	21,	11.287	24,	11.287
18,	11.279	22,	11.284	25,	11.292
19,	11.271				(10 days)

Mean total pressure, Oct. 16–25 = 11.285 atms.
Mean barom. pressure, Oct. 16–25 = 1.000 atm.
Mean osmot. pressure, Oct. 16–25 = 10.285 atms.
Mean osmotic pressure of Expts. 1 and 2 = 10.295 atms.
Ratio of osmotic to gas pressure = 1.040.

Table XXXVI

0.4 Wt. normal solution. Expt. 1 at 40°. Cell D_3. Resistance, 126,000 ohms. Manometer 15. Calc. gas pressure, 10.213 atms. Time of setting up cell, March 14, 1911. Barometer during final record: max., 1.014; min., 0.977. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 15,	10.345	Mar. 18,	11.510	Mar. 20,	11.512
16,	11.047	19,	11.512	21,	11.517
17,	11.370				

Final Record

	Atms.		Atms.		Atms.
Mar. 22,	11.605	Mar. 25,	11.586	Mar. 28,	11.581
23,	11.596	26,	11.566	29,	11.614
24,	11.609	27,	11.599	30,	11.575

Mean total pressure, Mar. 22–30 = 11.593 atms.
Mean barom. pressure, Mar. 22–30 = 0.994 atm.
Mean osmot. pressure, Mar. 22–30 = 10.599 atms.

Table XXXVII

0.4 Wt. normal solution. Expt. 2 at 40°. Cell R_2. Resistance, 205,000 ohms. Manometer 9. Calc. gas pressure, 10.213 atms. Time of setting up cell, March 14, 1911. Barometer during final record: max., 1.011; min., 0.990. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 16,	11.617	Mar. 18,	11.592	Mar. 19,	11.606
17,	11.603				

Mean total pressure, Mar. 16–19 = 11.6045 atms.
Mean barom. pressure, Mar. 16–19 = 1.002 atms.
Mean osmot. pressure, Mar. 16–19 = 10.6025 atms.

Table XXXVIII

0.4 Wt. normal solution. Expt. 3 at 40°. Cell N_3. Resistance, 190,000 ohms. Manometer 6. Calc. gas pressure, 10.213 atms. Time of setting up cell, March 14, 1911. Barometer during final record: max., 1.016; min., 0.990. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 15,	14.135	Mar. 18,	12.292	Mar. 20,	11.724
16,	13.359	19,	11.838	21,	(not rec'd)
17,	12.770				

Final Record

	Atms.		Atms.		Atms.
Mar. 22,	11.612	Mar. 24,	11.620	Mar. 26,	11.615
23,	11.583	25,	11.621	27,	11.607

Mean total pressure, Mar. 22–27 = 11.6097 atms.
Mean barom. pressure, Mar. 22–27 = 1.003 atms.
Mean osmot. pressure, Mar. 22–27 = 10.6067 atms.

Table XXXIX

0.4 Wt. normal solution. Expt. 4 at 40°. Cell I_4. Resistance, 120,000 ohms. Manometer 5. Calc. gas pressure, 10.213 atms. Time of setting up cell, March 11, 1911. Barometer during final record: max., 1.012; min., 0.992. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 12,	11.562	Mar. 15,	11.568	Mar. 17,	11.567
13,	11.621	16,	11.596	18,	11.577
14,	11.621				

Mean total pressure, Mar. 12–18 = 11.5874 atms.
Mean barom. pressure, Mar. 12–18 = 1.001 atms.
Mean osmot. pressure, Mar. 12–18 = 10.5864 atms.
Mean osmotic pressure for Expts. 1, 2, 3 and 4 = 10.5987 atms.
Ratio of osmotic to gas pressure = 1.0377

Table XL

0.4 Wt. normal solution. Expt. 1 at 50°. Cell S_3. Resistance, 71,000 ohms. Manometer 38. Calc. gas pressure, 10.540 atms. Time of setting up cell, January 4, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 5,	13.451	Jan. 7,	12.088	Jan. 9,	11.878
6,	12.838	8,	(not rec'd)	10,	11.833

Final Record

	Atms.		Atms.		Atms.
Jan. 11,	11.750	Jan. 15,	11.742	Jan. 18,	11.731
12,	11.759	16,	11.738	19,	11.725
13,	11.750	17,	11.732	20,	11.726
14,	11.748				(10 days)

Mean total pressure, Jan. 11–20 = 11.740 atms.
Mean barom. pressure, Jan. 11–20 = 1.003 atms.
Mean osmot. pressure, Jan. 11–20 = 10.737 atms.

Table XLI

0.4 Wt. normal solution. Expt. 2 at 50°. Cell H_3. Resistance, 190,000 ohms. Manometer 4. Calc. gas pressure, 10.540 atms. Time of setting up cell, January 4, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 5,	12.309	Jan. 7,	11.906	Jan. 9,	10.827
6,	11.955	8,	11.853	10,	(not rec'd)

Final Record

	Atms.		Atms.		Atms.
Jan. 11,	11.695	Jan. 15,	11.724	Jan. 18,	11.711
12,	11.704	16,	11.711	19,	11.702
13,	11.718	17,	11.713	20,	11.724
14,	11.729				(10 days)

Mean total pressure, Jan. 11–20 = 11.713 atms.
Mean barom. pressure, Jan. 11–20 = 1.003 atms.
Mean osmot. pressure, Jan. 11–20 = 10.710 atms.
Mean osmotic pressure for Expts. 1 and 2 = 10.724 atms
Ratio of osmotic to gas pressure = 1.017

Table XLII

0.4 Wt. normal solution. Expt. 1 at 60°. Cell G_5. Resistance, 28,000 ohms. Manometer 39. Calc. gas pressure, 10.867 atms. Time of setting up cell, February 12, 1912. Barometer during final record: max., 1.018; min., 0.983. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 13,	16.075	Feb. 17,	11.955	Feb. 20,	13.281
14,	13.964	18,	11.789	21,	12.043
15,	12.822	19,	14.031[1]	22,	12.040
16,	12.335				

Final Record

	Atms.		Atms.		Atms.
Feb. 23,	11.892	Feb. 27,	11.877	Mar. 2,	11.885
24,	11.858	28,	11.869	3,	11.886
25,	11.868	29,	11.874	4,	11.887
26,	11.853	Mar. 1,	11.886		(11 days)

Mean total pressure, Feb. 23–Mar. 4 = 11.876 atms.
Mean barom. pressure, Feb. 23–Mar. 4 = 1.005 atms.
Mean osmot. pressure, Feb. 23–Mar. 4 = 10.871 atms.

Table XLIII

0.4 Wt. normal solution. Expt. 2 at 60°. Cell F_3. Resistance, 57,500 ohms. Manometer 5. Calc. gas pressure, 10.867 atms. Time of setting up cell, February 26, 1912. Barometer during final record: max., 1.018; min., 0.994. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 27,	11.578	Feb. 29,	12.744[2]	Mar. 2,	11.948
28,	11.394	Mar. 1,	12.176		

Final Record

	Atms.		Atms.		Atms.
Mar. 3,	11.889	Mar. 6,	11.858	Mar. 9,	11.850
4,	11.862	7,	11.848	10,	11.862
5,	11.882	8,	11.827	11,	11.858

Mean total pressure, Mar. 3–11 = 11.860 atms.
Mean barom. pressure, Mar. 3–11 = 1.007 atms.
Mean osmot. pressure, Mar. 3–11 = 10.853 atms.

[1] Manometer cone screwed down.
[2] Cone tightened.

Table XLIV

0.4 Wt. normal solution. Expt. 3 at 60°. Cell C_3. Resistance, 16,000 ohms. Manometer 2. Calc. gas pressure, 10.867 atms. Time of setting up cell, February 26, 1912. Barometer during final record: max., 1.018; min., 0.994. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Feb. 29,	11.900	Mar. 4,	11.863	Mar. 7,	11.886
Mar. 1,	11.858	5,	11.877	8,	11.890
2,	11.891	6,	11.890	9,	11.880
3,	11.890				(10 days)

Mean total pressure, Feb. 29–Mar. 9 = 11.883 atms.
Mean barom. pressure, Feb. 29–Mar. 9 = 1.010 atms.
Mean osmot. pressure, Feb. 29–Mar. 9 = 10.873 atms.
Mean osmotic pressure for Expts. 1, 2 and 3 = 10.866 atms.
Ratio of osmotic to gas pressure = 1.000

Table XLV

0.5 Wt. normal solution. Expt. 1 at 30°. Cell I_5. Resistance, 110,000 ohms. Manometer 4. Calc. gas pressure, 12.358 atms. Time of setting up cell, October 10, 1911. Barometer during final record: max., 1.014; min., 0.989. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Oct. 11,	16.618	Oct. 13,	14.771	Oct. 15,	14.169
12,	15.442	14,	14.452	16,	14.097

Final Record

	Atms.		Atms.		Atms.
Oct. 17,	13.996	Oct. 20,	13.974	Oct. 23,	13.974
18,	13.976	21,	13.976	24,	13.990
19,	13.966	22,	13.972	25,	14.000

Mean total pressure, Oct. 17–25 = 13.9804 atms.
Mean barom. pressure, Oct. 17–25 = 1.000 atm.
Mean osmot. pressure, Oct. 17–25 = 12.9804 atms.

Table XLVI

0.5 Wt. normal solution. Expt. 2 at 30°. Cell O_3. Resistance, 100,000 ohms. Manometer 15. Calc. gas pressure, 12.358 atms. Time of setting up cell, October 19, 1911. Barometer during final record: max., 1.014; min., 0.995. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 21,	13.962	Oct. 25,	13.986	Oct. 28,	13.986
22,	13.971	26,	13.981	29,	13.981
23,	13.975	27,	13.982	30,	13.981
24,	13.979				(10 days)

Mean total pressure, Oct. 21–30 = 13.9784 atms.
Mean barom. pressure, Oct. 21–30 = 1.003 atms.
Mean osmot. pressure, Oct. 21–30 = 12.9754 atms.
Mean osmotic pressure for Expts. 1 and 2 = 12.9779 atms.
Ratio of osmotic to gas pressure = 1.050

Table XLVII

0.5 Wt. normal solution. Expt. 1 at 40°. Cell A_3. Resistance, 100,000 ohms. Manometer 9. Calc. gas pressure, 12.767 atms. Time of setting up cell, March 29, 1911. Barometer during final record: max., 1.009; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 31,	14.359	Apr. 2,	14.338	Apr. 3,	14.334
Apr. 1,	14.363				

Mean total pressure, Mar. 31–Apr. 3 = 14.349 atms.
Mean barom. pressure, Mar. 31–Apr. 3 = 1.000 atm.
Mean osmot. pressure, Mar. 31–Apr. 3 = 13.349 atms.

Table XLVIII

0.5 Wt. normal solution. Expt. 2 at 40°. Cell B_3. Resistance, 80,000 ohms. Manometer 24. Calc. gas pressure, 12.767 atms. Time of setting up cell, March 29, 1911. Barometer during final record: max., 1.009; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 31,	14.346	Apr. 2,	14.381	Apr. 3,	14.378
Apr. 1,	14.338				

Mean total pressure, Mar. 31–Apr. 3 = 14.361 atms.
Mean barom. pressure, Mar. 31–Apr. 3 = 1.000 atms.
Mean osmot. pressure. Mar. 31–Apr. 3 = 13.361 atms.
Mean osmotic pressure for Expts. 1 and 2 = 13.355 atms.
Ratio of osmotic to gas pressure = 1.046

Table XLIX

0.5 Wt. normal solution. Expt. 1 at 50°. Cell I_3. Resistance, 81,000 ohms. Manometer 1. Calc. gas pressure, 13.175 atms. Time of setting up cell, January 4, 1912. Barometer: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 5,	18.777	Jan. 7,	14.916	Jan. 9,	(not rec'd)
6,	15.851	8,	14.831		

Final Record

	Atms.		Atms.		Atms.
Jan. 10,	14.534	Jan. 14,	14.501	Jan. 17,	14.493
11,	14.511	15,	14.512	18,	14.496
12,	14.541	16,	14.527	19,	14.512
13,	14.541				(10 days)

Mean total pressure, Jan. 10–19 = 14.5168 atms.
Mean barom. pressure, Jan. 10–19 = 1.002 atms.
Mean osmot. pressure, Jan. 10–19 = 13.5148 atms.

Table L

0.5 Wt. normal solution. Expt. 2 at 50°. Cell F_3. Resistance, 377,000 ohms. Manometer 29. Calc. gas pressure, 13.175 atms. Time of setting up cell, January 4, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 5,	18.764	Jan. 7,	16.267	Jan. 9,	(not rec'd)
6,	17.088	8,	15.757		

Final Record

	Atms.		Atms.		Atms.
Jan. 10,	14.416	Jan. 14,	14.515	Jan. 17,	14.524
11,	14.451	15,	14.513	18,	14.518
12,	14.487	16,	14.520	19,	14.504
13,	14.499				(10 days)

Mean total pressure, Jan. 10–19 = 14.4947 atms.
Mean barom. pressure, Jan. 10–19 = 1.002 atms.
Mean osmot. pressure, Jan. 10–19 = 13.4927 atms.

Table LI

0.5 Wt. normal solution. Expt. 3 at 50°. Cell L_3. Resistance, 94,000 ohms. Manometer 9. Calc. gas pressure, 13.175 atms. Time of setting up cell, January 4, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

	Atms.		Atms.		
Jan. 5,	(not rec'd)	Jan. 7,	14.584	Jan. 9	(not rec'd)
6,	"	8,	14.500		

Final Record

	Atms.		Atms.		Atms.
Jan. 10,	14.435	Jan. 14,	14.526	Jan. 17,	14.518
11,	14.487	15,	14.511	18,	14.522
12,	14.522	16,	14.524	19,	14.508
13,	14.504				(10 days)

Mean total pressure, Jan. 10–19 = 14.5057 atms.
Mean barom. pressure, Jan. 10–19 = 1.002 atms.
Mean. osmot. pressure, Jan. 10–19 = 13.5037 atms.
Mean osmotic pressure for Expts. 1, 2 and 3 = 13.5037 atms.
Ratio of osmotic to gas pressure = 1.025

Table LII

0.5 Wt. normal solution. Expt. 1 at 60°. Cell V_3. Resistance, 11,600 ohms. Manometer 31. Calc. gas pressure, 13.584 atms. Time of setting up cell, Feb. 23, 1912. Barometer during final record: max., 1.018; min., 0.994. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Feb. 24,	19.002	Feb. 27,	16.210	Feb. 29,	14.852
25,	17.101	28,	15.059	Mar. 1,	14.730
26,	17.002				

Final Record

	Atms.		Atms.		Atms.
Mar. 2,	14.654	Mar. 6,	14.646	Mar. 10,	14.649
3,	14.654	7,	14.643	11,	14.654
4,	14.645	8,	14.688	12,	14.655
5,	14.634	9,	14.661		(11 days)

Mean total pressure, Mar. 2–12 = 14.653 atms.
Mean barom. pressure, Mar. 2–12 = 1.008 atms.
Mean osmot. pressure, Mar. 2–12 = 13.645 atms.

Table LIII

0.5 Wt. normal solution. Expt. 2 at 60°. Cell C_5. Resistance, 50,000 ohms. Manometer 4. Calc. gas pressure, 13.584 atms. Time of setting up cell, March 15, 1912. Barometer during final record: max., 1.014; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 18,	14.637	Mar. 22,	14.759	Mar. 25,	14.703
19,	14.608	23,	14.773	26,	14.707
20,	14.620	24,	14.724	27,	14.707
21,	14.635				(10 days)

Mean total pressure, Mar. 18–27 = 14.6873 atms.
Mean barom. pressure, Mar. 18–27 = 1.000 atm.
Mean osmot. pressure, Mar. 18–27 = 13.6873 atms.
Mean osmotic pressure for Expts. 1 and 2 = 13.662 atms.
Ratio of osmotic to gas pressure = 1.0057

Table LIV

0.5 Wt. normal solution. Expt. 1 at 70°. Cell E_5. Resistance, 13,000 ohms. Manometer 1. Calc. gas pressure, 13.992 atms. Time of setting up cell, May 13, 1912. Barometer during final record: max., 1.005; min., 0.982. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 16,	15.015	May 18,	14.985	May 20,	14.974
17,	14.986	19,	14.978		

Mean total pressure, May 16–20 = 14.988 atms.
Mean barom. pressure, May 16–20 = 0.994 atms.
Mean osmot. pressure, May 16–20 = 13.994 atms.

Table LV

0.5 Wt. normal solution. Expt. 2 at 70°. Cell L_5. Resistance, 9,600 ohms. Manometer 38. Calc. gas pressure, 13.992 atms. Time of setting up cell, May 13, 1912. Barometer during final record: max., 1.004; min., 0.982. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 15,	14.993	May 17,	14.981	May 19,	14.981
16,	14.984	18,	14.979	20,	14.985

Mean total pressure, May 15–20 = 14.984 atms.
Mean barom. pressure, May 15–20 = 0.994 atm.
Mean osmot. pressure, May 15–20 = 13.990 atms.
Mean osmotic pressure for Expts. 1 and 2 = 13.9905 atms.
Ratio of osmotic to gas pressure = 1.000

Table LVI

0.6 Wt. normal solution. Expt. 1 at 30°. Cell 105. Resistance, 250,000 ohms. Manometer 24. Calc. gas pressure, 14.830 atms. Time of setting up cell, Oct. 5, 1911. Barometer during final record: max., 1.008; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 7,	16.672	Oct. 10,	16.702	Oct. 12,	16.693
8,	16.771	11,	16.694	13,	16.699
9,	16.713				(7 days)

Mean total pressure, Oct. 7–13 = 16.706 atms.
Mean barom. pressure, Oct. 7–18 = 1.000 atm.
Mean osmot. pressure, Oct. 7–13 = 15.706 atms.

Table LVII

0.6 Wt. normal solution. Expt. 2 at 30°. Cell H_3. Reistance, 200,000 ohms. Manometer 15. Calc. gas pressure, 14.830 atms. Time of setting up cell, Oct. 5, 1911. Barometer during final record: max., 1.008; min., 0.993. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 9,	16.733	Oct. 13,	16.688	Oct. 16,	16.691
10,	16.698	14,	16.683	17,	16.688
11,	16.691	15,	16.684	18,	16.688
12,	16.693				(10 days)

Mean total pressure, Oct. 9–18 = 16.6937 atms.
Mean barom. pressure, Oct. 9–18 = 1.000 atm.
Mean osmot. pressure, Oct. 9–18 = 15.6937 atms.

Table LVIII

0.6 Wt. normal solution. Expt. 3 at 30°. Cell 110. Resistance, 150,000 ohms. Manometer 29. Calc. gas pressure, 14.830 atms. Time of setting up cell, Oct. 5, 1911. Barometer during final record: max., 1.008; min., 0.993. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 7,	16.734	Oct. 10,	16.772	Oct. 12,	16.752
8,	16.790	11,	16.760	13,	16.751
9,	16.782				(7 days)

Mean total pressure, Oct. 7–13 = 16.763 atms.
Mean barom. pressure, Oct. 7–13 = 1.000 atm.
Mean osmot. pressure, Oct. 7–13 = 15.763 atms.

Table LIX

0.6 Wt. normal solution. Expt. 4 at 30°. Cell B_5. Resistance, 200,000 ohms. Manometer 9. Calc. gas pressure, 14.830 atms. Time of setting up cell, Oct. 5, 1911. Barometer during final record: max., 1.008; min., 0.993. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Oct. 10,	16.704	Oct. 12,	16.698	Oct. 13,	16.665
11,	16.693				

Mean total pressure, Oct. 10–13 = 16.690 atms.
Mean barom. pressure, Oct. 10–13 = 1.000 atm.
Mean osmot. pressure, Oct. 10–13 = 15.690 atms.
Mean osmotic pressure for Expts. 1, 2, 3 and 4 = 15.7132 atms.
Ratio of osmotic to gas pressure = 1.0595

Table LX

0.6 Wt. normal solution. Expt. 1 at 40°. Cell H_5. Resistance, 110,000 ohms. Manometer 6. Calc. gas pressure, 15.320 atms. Time of setting up cell, March 9, 1911. Barometer during final record: max., 1.009; min., 0.997. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 11,	17.138	Mar. 13,	17.150	Mar. 14,	17.144
12,	17.153				(4 days)

Mean total pressure, Mar. 11–14 = 17.141 atms.
Mean barom. pressure, Mar. 11–14 = 1.004 atms.
Mean osmot. pressure, Mar. 11–14 = 16.137 atms.

Table LXI

0.6 Wt. normal solution. Expt. 2 at 40°. Cell E_5. Resistance, 110,000 ohms. Calc. gas pressure, 15.320 atms. Manometer 9. Time of setting up cell, March 9, 1911. Barometer during final record: max., 1.009; min., 0.997. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 12,	17.150	Mar. 13,	17.159	Mar. 14,	17.161

Mean total pressure, Mar. 12–14 = 17.157 atms.
Mean barom. pressure, Mar. 12–14 = 1.003 atms.
Mean osmot. pressure, Mar. 12–14 = 16.154 atms.
Mean osmotic pressure for Expts. 1 and 2 = 16.146 atms.
Ratio of osmotic to gas pressure = 1.054

Table LXII

0.6 Wt. normal solution. Expt. 1 at 50°. Cell C_3. Resistance, 59,000 ohms. Manometer 31. Calc. gas pressure, 15.810 atms. Time of setting up cell, January 5, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Jan. 10,	17.322	Jan. 15,	17.318	Jan. 19,	17.318
11,	17.339	16,	17.323	20,	17.320
12,	17.332	17,	17.318	21,	17.324
13,	17.333	18,	17.320	22,	17.320
14,	17.337				(13 days)

Mean total pressure, Jan. 10–22 = 17.325 atms.
Mean barom. pressure, Jan. 10–22 = 1.003 atms.
Mean osmot. pressure, Jan. 10–22 = 16.322 atms.

Table LXIII

0.6 Wt. normal solution. Expt. 2 at 50°. Cell R_5. Resistance, 118,000 ohms. Manometer 5. Calc. gas pressure, 15.810 atms. Time of setting up cell, January 5, 1912. Barometer during final record: max., 1.019; min., 0.988. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Jan. 6,	18.177	Jan. 8,	17.532	Jan. 10,	17.089
7,	18.742	9,	16.945	11,	17.172

Final Record

	Atms.		Atms.		Atms.
Jan. 12,	17.302	Jan. 16,	17.309	Jan. 20,	17.316
13,	17.296	17,	17.313	21,	17.313
14,	17.321	18,	17.302	22,	17.312
15,	17.313	19,	17.301		(11 days)

Mean total pressure, Jan. 12–22 = 17.309 atms.
Mean. barom. pressure, Jan. 12–22 = 1.003 atms.
Mean osmot. pressure, Jan. 12–22 = 16.306 atms.
Mean osmotic pressure for Expts. 1 and 2 = 16.319 atms.
Ratio of osmotic to gas pressure = 1.032

Table LXIV

0.6 Wt. normal solution. Expt. 1 at 60°. Cell R_3. Resistance, 29,000 ohms. Manometer 11. Calc. gas pressure, 16.300 atms. Time of setting up cell, March 6, 1912. Barometer during final record: max., 1.015; min., 0.985. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 7,	22.343	Mar. 9,	17.912	Mar. 11,	17.092
8,	19.050	10,	16.804	12,	17.343

Final Record

	Atms.		Atms.		Atms.
Mar. 13,	17.487	Mar. 16,	17.499	Mar. 19,	17.517
14,	17.498	17,	17.485	20,	17.546
15,	17.578	18,	17.522	21,	17.531

Mean total pressure, Mar. 13–21 = 17.518 atms.
Mean barom. pressure, Mar. 13–21 = 0.999 atm.
Mean osmot. pressure, Mar. 13–21 = 16.519 atms.

Table LXV

0.6 Wt. normal solution. Expt. 2 at 60°. Cell P_3. Resistance, 23,000 ohms. Manometer 5. Calc. gas pressure, 16.300 atms. Time of setting up cell, March 6, 1912. Barometer during final record: max., 1.015; min., 0.985. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 7,	18.627	Mar. 9,	17.301	Mar. 11,	17.262
8,	17.699	10,	16.454	12,	17.358

Final Record

	Atms.		Atms.		Atms.
Mar. 13,	17.555	Mar. 16,	17.553	Mar. 19,	17.527
14,	17.616	17,	17.523	20,	17.523
15,	17.585	18,	17.553	21,	17.519

Mean total pressure, Mar. 13–21 = 17.550 atms.
Mean. barom. pressure, Mar. 13–21 = 0.999 atm.
Mean osmot. pressure, Mar. 13–21 = 16.551 atms.
Mean osmotic pressure for Expts. 1 and 2 = 16.535 atms.
Ratio of osmotic to gas pressure = 1.014

Table LXVI

0.6 Wt. normal solution. Expt. 1 at 70°. Cell B_3. Resistance, 10,000 ohms. Manometer 31. Calc. gas pressure, 16.790 atms. Time of setting up cell, May 10, 1912. Barometer during final record: max., 1.002; min., 0.985. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 11,	17.812	May 13,	17.824	May 15,	17.800
12,	17.820	14,	17.816	16,	17.795

Mean total pressure, May 11–17 = 17.810 atms.
Mean barom. pressure, May 11–17 = 0.995 atm.
Mean osmot. pressure, May 11–17 = 16.815 atms.

Table LXVII

0.6 Wt. normal solution. Expt. 2 at 70°. Cell W_5. Resistance, 16,400 ohms. Manometer 15. Calc. gas pressure, 16.790 atms. Time of setting up cell, May 9, 1912. Barometer during final record: max., 1.004; min., 0.982. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 13,	17.859	May 15,	17.817	May 17	17.817
14.	17.822	16,	17.801	18,	17.800

Mean total pressure, May 13–18 = 17.819 atms.
Mean barom. pressure, May 13–18 = 0.995 atm.
Mean osmot. pressure, May 13–18 = 16.824 atms.
Mean osmotic pressure for Expts. 1 and 2 = 16.8195 atms.
Ratio of osmotic to gas pressure = 1.0018.

Table LXVIII

0.7 Wt. normal solution. Expt. 1 at 30°. Cell H_3. Resistance, 225,000 ohms. Manometer 24. Calc. gas pressure, 17.301 atms. Time of setting up cell, May 30, 1911. Barometer during final record: max., 1.004; min., 0.990. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
June 3,	19.505	June 7,	19.497	June 10,	19.483
4,	19.490	8,	19.497	11,	19.483
5,	19.487	9,	19.505	12,	19.483
6,	19.487				(10 days)

Mean total pressure, June 3–12 = 19.4917 atms.
Mean barom. pressure, June 3–12 = 0.998 atm.
Mean osmot. pressure, June 3–12 = 18.4937 atms.

Table LXIX

0.7 Wt. normal solution. Expt. 2 at 30°. Cell B_3. Resistance, 110,000 ohms. Manometer 9. Calc. gas pressure, 17.301 atms. Time of setting up cell, June 3, 1911. Barometer during final record: max., 1.004; min., 0.990. Total daily pressures:

Final Record

	Atms.		Atms.		Atms
June 5,	19.524	June 8,	19.510	June 11,	19.482
6,	19.514	9,	19.496	12,	19.490
7,	19.507	10,	19.490		(8 days)

Mean total pressure, June 5–12 = 19.5016 atms.
Mean. barom. pressure, June 5–12 = 0.997 atm.
Mean osmot. pressure, June 5–12 = 18.5046 atms.
Mean osmotic pressure for Expts. 1 and 2 = 18.4992 atms.
Ratio of osmotic to gas pressure = 1.069

Table LXX

0.7 Wt. normal solution. Expt. 1 at 40°. Cell A_3. Resistance, 90,000 ohms. Manometer 6. Calc. gas pressure, 17.873 atms. Time of setting up cell, May 9, 1911. Barometer during final record: max., 1.005; min., 0.994. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 13,	19.943	May 15,	19.999	May 17,	19.960
14,	(not rec'd)	16,	19.956	18,	19.947

Mean total pressure, May 13–18 = 19.961 atms.
Mean barom. pressure, May 13–18 = 0.999 atm.
Mean osmot. pressure, May 13–18 = 18.962 atms.

Table LXXI

0.7 Wt. normal solution. Expt. 2 at 40°. Cell C_3. Resistance, 110,000 ohms. Manometer 24. Calc. gas pressure, 17.873 atms. Time of setting up cell, May 12, 1911. Barometer during final record: max., 1.010; min., 0.994. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 13,	19.934	May 15,	19.892	May 17,	19.900
14,	19.895	16,	19.887	18,	19.911

Mean total pressure, May 13–18 = 19.902 atms.
Mean barom. pressure, May 13–18 = 1.001 atms.
Mean osmot. pressure, May 13–18 = 18.901 atms.
Mean osmotic pressure for Expts. 1 and 2 = 18.932 atms.
Ratio of osmotic to gas pressure = 1.0592

Table LXXII

0.7 Wt. normal solution. Expt. 1 at 50°. Cell D_4. Resistance, 110,-009 ohms. Manometer 29. Calc. gas pressure, 18.445 atms. Time of setting up cell, December 14, 1911. Barometer during final record: max., 1.003; min., 0.981. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 15,	25.092	Dec. 18,	22.417	Dec. 21,	20.464
16,	25.508	19,	21.285	22,	20.392
17,	23.246	20,	20.727		

Final Record

	Atms.		Atms.		Atms.
Dec. 23,	20.272	Dec. 25,	20.211	Dec. 27,	20.194
24,	20.237	26,	20.211	28,	20.198

Mean total pressure, Dec. 23–28 = 20.2205 atms.
Mean barom pressure, Dec. 23–28 = 0.996 atm.
Mean osmot. pressure, Dec. 23–28 = 19.2245 atms.

Table LXXIII

0.7 Wt. normal solution. Expt. 2 at 50°. Cell Z_2. Resistance, 150,-000 ohms. Manometer 4. Calc. gas pressure, 18.445 atms. Time of setting up cell, December 14, 1911. Barometer during final record: max., 1.003; min., 0.981. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Dec. 16,	21.728	Dec. 18,	20.601	Dec. 20,	19.652
17,	20.597	19,	19.554	21,	19.869

Final Record

	Atms.		Atms.		Atms.
Dec. 22,	20.297	Dec. 25,	20.178	Dec. 27,	20.143
23,	20.103	26,	20.164	28,	20.164
24,	20.186				

Mean total pressure, Dec. 22–28 = 20.1764 atms.
Mean barom. pressure, Dec. 22–28 = 0.997 atm.
Mean osmot. pressure, Dec. 22–28 = 19.1794 atms.
Mean osmotic pressure for Expts. 1 amd 2 = 19.2019 atms.
Ratio of osmotic to gas pressure = 1.041

Table LXXIV

0.7 Wt. normal solution. Expt. 1 at 60°. Cell Z_5. Resistance, 27,000 ohms. Manometer 39. Calc. gas pressure, 19.017 atms. Time of setting up cell, March 14, 1912. Barometer during final record: max., 1.014; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 19,	20.319	Mar. 23,	20.450	Mar. 26,	20.438
20,	20.357	24,	20.444	27,	20.426
21,	20.362	25,	20.441	28,	20.410
22,	20.371				(10 days)

Mean total pressure, March 19–28 = 20.4018 atms.
Mean barom. pressure, March 19–28 = 0.999 atm.
Mean osmot. pressure, March 19–28 = 19.4028 atms.

Table LXXV

0.7 Wt. normal solution. Expt. 2 at 60°. Cell A_5. Resistance, 58,000 ohms. Manometer 31. Calc. gas pressure, 19.017 atms. Time of setting up cell, March 14, 1912. Barometer during final record: max., 1.014; min., 0.974. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 15,	24.111	Mar. 18,	21.524	Mar. 20,	20.770
16,	23.161	19,	21.118	21,	20.552
17,	21.879				(7 days)

Final Record

	Atms.		Atms.		Atms.
Mar. 22,	20.428	Mar. 26,	20.400	Mar. 30,	20.395
23,	20.409	27,	20.390	31,	20.395
24,	20.417	28,	20.400	Apr. 1,	20.395
25,	20.416	29,	20.395		(11 days)

Mean total pressure, March 22–April 1 = 20.4036 atms.
Mean barom. pressure, March 22–April 1 = 0.999 atm.
Mean osmot. pressure, March 22–April 1 = 19.4046 atms.
Mean osmotic pressure for Expts. 1 and 2 = 19.4037 atms.
Ratio of osmotic to gas pressure = 1.020

Table LXXVI

0.7 Wt. normal solution. Expt. 1 at 70°. Cell J_3. Resistance, 8,000 ohms. Manometer 38. Calc. gas pressure, 19.587 atms. Time of setting up cell, May 2, 1912. Barometer during final record: max., 0.998; min., 0.984. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
May 3,	19.933	May 5,	20.154	May 7,	20.035
4,	21.154	6,	20.446		

Final Record

	Atms.		Atms.		Atms.
May 8,	20.557	May 10,	20.516	May 12,	20.528
9,	20.564	11,	20.516	13,	20.534

Mean total pressure, May 8–13 = 20.543 atms.
Mean barom. pressure, May 8–13 = 0.990 atms.
Mean osmot. pressure, May 8–13 = 19.553 atms.

Table LXXVII

0.7 Wt. normal solution. Expt. 2 at 70°. Cell F_3. Resistance, 10,000 ohms. Manometer 24. Calc. gas pressure, 19.589 atms. Time of setting up cell, May 11, 1912. Barometer during final record: max., 1.004; min., 0.982. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 13,	20.559	May 15,	20.600	May 17,	20.578
14,	20.574	16,	20.592	18,	20.566

Mean total pressure, May 13–18 = 20.577 atms.
Mean barom. pressure, May 13–18 = 0.994 atm.
Mean osmot. pressure, May 13–18 = 19.583 atms.
Mean osmotic pressure for Expts. 1 and 2 = 19.568 atms.
Ratio of osmotic to gas pressure = 0.999

Table LXXVIII

0.8 Wt. normal solution. Expt. 1 at 30°. Cell C_3. Resistance, 220,000 ohms. Manometer 29. Calc. gas pressure, 19.773 atms. Time of setting up cell, May 26, 1911. Barometer during final record: max., 1.002; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 29,	22.421	May 31,	22.392	June 2,	22.381
30,	22.392	June 1,	22.396	3,	22.387

Mean total pressure, May 29–June 3 = 22.395 atms.
Mean barom. pressure, May 29–June 3 = 0.999 atm.
Mean osmot. pressure, May 29–June 3 = 21.396 atms.

Table LXXIX

0.8 Wt. normal solution. Expt. 2 at 30°. Cell A_3. Resistance, 110,000 ohms. Manometer 9. Calc. gas pressure, 19.773 atms. Time of setting up cell, May 26, 1911. Barometer during final record: max., 1.003; min., 0.989.

Final Record

	Atms.		Atms.		Atms.
May 28,	22.389	May 31,	22.347	June 2,	22.342
29,	22.361	June 1,	22.342	3,	22.352
30,	22.339				

Mean total pressure, May 28–June 3 = 22.353 atms.
Mean barom. pressure, May 28–June 3 = 0.999 atm.
Mean osmot. pressure, May 28–June 3 = 21.354 atms.
Mean osmotic pressure for Expts. 1 and 2 = 21.375 atms.
Ratio of osmotic to gas pressure = 1.081

Table LXXX

0.8 Wt. normal solution. Expt. 1 at 40°. Cell I_3. Resistance, 100,000 ohms. Manometer 5. Calc. gas pressure, 20.426 atms. Time of setting up cell, February 23, 1911. Barometer during final record: max., 1.009; min., 0.988. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Feb. 27,	22.779	Mar. 1,	22.780	Mar. 2,	22.767
28,	22.788				

Mean total pressure, Feb. 27–Mar. 2 = 22.779 atms.
Mean barom. pressure, Feb. 27–Mar. 2 = 1.000 atm.
Mean osmot. pressure, Feb. 27–Mar. 2 = 21.779 atms.

Table LXXXI

0.8 Wt. normal solution. Expt. 2 at 40°. Cell A_3. Resistance, 225,000 ohms. Manometer 9. Calc. gas pressure, 20.426 atms. Time of setting up cell, March 3, 1911. Barometer during final record: max., 1.016; min., 1.006. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 7,	22.831	Mar. 8,	22.817	Mar. 9,	22.822

Mean total pressure, Mar. 7–9 = 22.823 atms.
Mean barom. pressure, Mar. 7–9 = 1.010 atms.
Mean osmot. pressure, Mar. 7–9 = 21.813 atms.

Table LXXXII

0.8 Wt. normal solution. Expt. 3 at 40°. Cell B_5. Resistance, 220,000 ohms. Manometer 6. Calc. gas pressure, 20.426 atms. Time of setting up cell, March 3, 1911. Barometer during final record: max., 1.016; min., 0.999. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 4,	22.859	Mar. 6,	22.842	Mar. 8,	22.842
5,	22.768	7,	22.813	9,	22.836

Meam total pressure, Mar. 4–9 = 22.827 atms.
Mean barom. pressure, Mar. 4–9 = 1.008 atms.
Mean osmot. pressure, Mar. 4–9 = 22.819 atms.

Table LXXXIII

0.8 Wt. normal solution. Expt. 4 at 40°. Cell D_5. Resistance, 333,000 ohms. Manometer 22. Calc. gas pressure, 20.426 atms. Time of setting up cell, March 3, 1911. Barometer during final record: max., 1.018; min., 0.999. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 4,	22.788	Mar. 6,	22.823	Mar. 8,	22.836
5,	22.800	7,	22.845	9,	22.829

Mean total pressure, March 4–9 = 22.820 atms.
Mean barom. pressure, March 4–9 = 1.009 atms.
Mean osmot. pressure, March 4–9 = 21.811 atms.
Mean osmotic pressure for Expts. 1, 2, 3 and 4 = 21.8028 atms.
Ratio of osmotic to gas pressure = 1.0674

Table LXXXIV

0.8 Wt. normal soln. Expt. 1 at 50°. Cell C_5. Resistance, 110,000 ohms. Manometer 28. Calc. gas pressure, 21.080 atms. Time of setting up cell, December 12, 1911. Barometer during final record: max., 1.014; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Dec. 13,	23.095	Dec. 18,	23.146	Dec. 23,	21.115
14,	23.116	19,	23.146	24,	23.075
15,	23.180	20,	23.158	25,	23.095
16,	23.164	21,	23.165	26,	23.115
17,	23.164	22,	23.135		(14 days)

Mean total pressure, Dec. 13–26 = 23.1335 atms.
Mean barom. pressure, Dec. 13–26 = 1.005 atms.
Mean osmot. pressure, Dec. 13–26 = 22.1285 atms.

Table LXXXV

0.8 Wt. normal solution. Expt. 2 at 50°. Cell J_5. Resistance, 100,000 ohms. Manometer 31. Calc. gas pressure, 21.080 atms. Time of setting up cell, December 12, 1911. Barometer during final record: max., 1.014; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Dec. 15,	23.069	Dec. 20,	23.149	Dec. 24,	23.103
16,	23.079	21,	23.131	25,	23.118
17,	23.068	22,	23.122	26,	23.107
18,	23.102	23,	23.107		
19,	23.135				(12 days)

Mean total pressure, Dec. 15–26 = 23.1075 atms.
Mean barom. pressure, Dec. 15–26 = 1.004 atms.
Mean osmot. pressure, Dec. 15–26 = 22.1035 atms.
Mean osmotic pressure for Expts. 1 and 2 = 22.116 atms.
Ratio of osmotic to gas pressure = 1.049.

Table LXXXVI

0.8 Wt. normal solution. Expt. 1 at 60°. Cell P_5. Resistance, 25,000 ohms. Manometer 1. Calc. gas pressure, 21.734 atms. Time of setting up cell, March 26, 1912. Barometer during final record: max., 1.012; min., 0.977. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 28,	23.358	Apr. 1,	23.345	Apr. 5,	23.348
29,	23.339	2,	23.339	6,	23.339
30,	23.348	3,	23.318	7,	23.325
31,	23.348	4,	23.357	8,	23.339
					(12 days)

Mean total pressure, Mar. 28–Apr. 8 = 23.342 atms.
Mean barom. pressure, Mar. 28–Apr. 8 = 0.998 atm.
Mean osmot. pressure, Mar. 28–Apr. 8 = 22.344 atms.

Table LXXXVII

0.8 Wt. normal solution. Expt. 2 at 60°. Cell E_5. Resistance, 20,000 ohms. Manometer 15. Calc. gas pressure, 21.734 atms. Time of setting up cell, March 26, 1912. Barometer during final record: max., 1.012; min., 0.977. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 30,	23.291	Apr. 3,	23.286	Apr. 7,	23.257
31,	(not rec'd)	4,	23.312	8,	23.349
Apr. 1,	23.329	5,	23.276	9,	23.345
2,	23.316	6,	23.298	10,	23.323
					(12 days)

Mean total pressure, March 30–April 10 = 23.308 atms.
Mean barom. pressure, March 30–April 10 = 0.998 atm.
Mean. osmot. pressure, March 30–April 10 = 22.310 atms.
Mean osmotic pressure for Expts. 1 and 2 = 22.327 atms.
Ratio of osmotic to gas pressure = 1.027

Table LXXXVIII

0.8 Wt. normal solution. Expt. 1 at 70°. Cell U_5. Resistance, 23,000 ohms. Manometer 31. Calc. gas pressure, 22.387 atms. Time of setting up cell, April 29, 1912. Barometer during final record: max., 0.998; min., 0.984. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 30,	25.575	May 2,	24.047	May 4,	23.628
May 1,	24.159	3,	23.810		

Final Record

May 5,	23.555	May 7,	23.547	May 9,	23.574
6,	23.549	8,	23.562	10,	23.568

Mean total pressure, May 5–10 = 23.559 atms.
Mean barom. pressure, May 5–10 = 0.992 atm.
Mean osmot. pressure, May 5–10 = 22.567 atms.

Table LXXXIX

0.8 Wt. normal solution. Expt. 2 at 70°. Cell R_3. Resistance, 10,000 ohms. Manometer 31. Calc. gas pressure, 22.387 atms. Time of setting up cell, May 16, 1912. Barometer during final record: max., 1.005; min., 1.001. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 18,	23.568	May 20,	23.556	May 22,	23.576
19,	23.565	21,	23.583		

Mean total pressure, May 18–22 = 23.570 atms.
Mean barom. pressure, May 18–22 = 1.003 atms.
Mean osmot. pressure, May 18–22 = 22.567 atms.
Mean osmotic pressure for Expts. 1 and 2 = 22.567 atms.
Ratio of osmotic to gas pressure = 1.008

Table XC

0.8 Wt. normal solution. Expt. 1 at 80°. Cell B_3. Resistance, 9,000 ohms. Manometer 24. Calc. gas pressure, 23.041 atms. Time of setting up cell, May 18, 1912. Barometer during final record: max., 1.004; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 22,	24.087	May 24,	24.042	May 25,	24.036
23,	24.073				

Mean total pressure, May 22–25 = 24.060 atms.
Mean barom. pressure, May 22–25 = 0.998 atm.
Mean osmot. pressure, May 22–25 = 23.062 atms.
Ratio of osmotic to gas pressure = 1.001

Table XCI

0.9 Wt. normal solution. Expt. 1 at 30°. Cell Z_3. Resistance, 250,000 ohms. Manometer 15. Calc. gas pressure, 22.244 atms. Time of setting up cell, October 29, 1910. Barometer during final record: max., 1.001; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 2,	25.249	Nov. 4,	(not rec'd)	Nov. 6,	25.194
3,	25.198	5,	25.214	7,	25.193

Mean total pressure, Nov. 2–7 = 25.2096 atms.
Mean barom. pressure, Nov. 2–7 = 0.995 atm.
Mean osmot. pressure, Nov. 2–7 = 24.2146 atms.

Table XCII

0.9 Wt. normal solution. Expt. 2 at 30°. Cell Co_1. Resistance of membrane (cobalt ferrocyanide), 240,000 ohms. Manometer 24. Calc. gas pressure, 22.244 atms. Time of setting up cell, May 24, 1911. Barometer during final record: max., 1.002; min., 0.997. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 26,	25.246	May 28,	25.245	May 30,	25.245
27,	25.227	29,	25.220	31,	25.245

Mean total pressure, May 26–31 = 25.238 atms.
Mean barom. pressure, May 26–31 = 1.000 atm.
Mean osmot. pressure, May 26–31 = 24.238 atms.
Mean osmotic pressure for Expts. 1 and 2 = 24.2263 atms.
Ratio of osmotic to gas pressure = 1.089

Table XCIII

0.9 Wt. normal solution. Expt. 1 at 40°. Cell Ni_2. Resistance of membrane (nickel ferrocyanide), 80,000 ohms. Manometer 29. Calc. gas pressure, 22.980 atms. Time of setting up cell, May 1, 1911. Barometer during final record: max., 1.010; min., 0.991. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
May 2,3,4,	(not rec'd)	May 8,	25.932	May 11,	25.477
5,	27.950	9,	(not rec'd)	12,	25.477
6,	26.336	10,	25.466	13,	25.582
7,	25.975				

Final Record

	Atms.		Atms.		Atms.
May 14,	25.701	May 16,	25.740	May 18,	25.743
15,	25.745	17,	25.737	19,	25.748

Mean total pressure, May 14–19 = 25.738 atms.
Mean barom. pressure, May 14–19 = 1.000 atm.
Mean osmot. pressure, May 14–19 = 24.738 atms.

Table XCIV

0.9 Wt. normal solution. Expt. 2 at 40°. Cell H_2. Resistance, 80,000 ohms. Manometer 9. Calc gas pressure, 22.980 atms. Time of setting up cell, May 1, 1911. Barometer during final record: max., 1.010; min., 0.986. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 4,	25.738	May 6,	25.751	May 8,	25.726
5,	25.720	7,	25.707	9,	25.745

Mean total pressure, May 4–9 = 25.731 atms.
Mean barom. pressure, May 4–9 = 1.001 atms.
Mean osmot. pressure, May 4–9 = 24.730 atms.

Table XCV

0.9 Wt. normal solution. Expt. 3 at 40°. Cell R_2. Resistance, 125,000 ohms. Manometer 22. Calc. gas pressure, 22.980 atms. Time of setting up cell, May 9, 1911. Barometer during final record: max., 1.010; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 14,	25.710	May 16,	25.718	May 18,	25.741
15,	25.763	17,	25.733	19,	25.761

Mean total pressure, May 14–19 = 25.738 atms.
Mean barom. pressure, May 14–19 = 1.000 atm.
Mean osmot. pressure, May 14–19 = 24.738 atms.
Mean osmotic pressure for Expts. 1, 2 and 3 = 24.735 atms.
Ratio of osmotic to gas pressure = 1.076

Table XCVI

0.9 Wt. normal solution. Expt. 1 at 50°. Cell G_2. Resistance, 100,000 ohms. Manometer 1. Calc. gas pressure, 23.715 atms. Time of setting up cell, November 22, 1911. Barometer during final record: max., 1.013; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 26,	26.103	Nov. 30,	26.115	Dec. 3,	26.127
27,	26.127	Dec. 1,	26.139	4,	26.150
28,	26.133	2,	26.161	5,	26.139
29,	26.127				(10 days)

Mean total pressure, Nov. 26–Dec. 5 = 26.132 atms.
Mean barom. pressure, Nov. 26–Dec. 5 = 1.000 atm.
Mean osmot. pressure, Nov. 26–Dec. 5 = 25.132 atms.

Table XCVII

0.9 Wt. normal solution. Expt. 2 at 50°. Cell F_3. Resistance, 100,000 ohms. Manometer 38. Calc. gas pressure, 23.715 atms. Time of setting up cell, Nov. 22, 1911. Barometer during final record: max., 1.013; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 26,	26.128	Nov. 30,	26.108	Dec. 3,	26.105
27,	26.142	Dec. 1,	26.082	4,	26.107
28,	26.127	2,	26.105	5,	26.108
29,	26.124				(10 days)

Mean total pressure, Nov. 26–Dec. 5 = 26.1136 atms.
Mean barom. pressure, Nov. 26–Dec. 5 = 1.000 atm.
Mean osmot. pressure, Nov. 26–Dec. 5 = 25.1136 atms.
Mean osmotic pressure for Expts. 1 and 2 = 25.1228 atms.
Ratio of osmotic to gas pressure = 1.0593

Table XCVIII

0.9 Wt. normal solution. Expt. 1 at 60°. Cell G_3. Resistance, 38,000 ohms. Manometer 28. Calc. gas pressure, 24.450 atms. Time of setting up cell, March 11, 1912. Barometer during final record: max., 1.014; min., 0.984. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Mar. 12,	33.353	Mar. 16,	25.902	Mar. 19,	25.856
13,	28.555	17,	25.753	20,	25.848
14.	26.730	18,	25.887	21,	25.850
15,	25.968				(10 days)

Final Record

	Atms.		Atms.		Atms.
Mar. 22,	26.208	Mar. 26,	26.260	Mar. 30,	26.269
23,	26.225	27,	26.262	31,	26.269
24,	26.237	28,	26.264	Apr. 1,	26.283
25,	26.250	29,	26.271		(11 days)

Mean total pressure, Mar. 22–Apr. 1 = 26.2544 atms.
Mean. barom. pressure, Mar. 22–Apr. 1 = 0.998 atm.
Mean osmot. pressure, Mar. 22–Apr. 1 = 25.2564 atms.

Table XCIX

0.9 Wt. normal solution. Expt. 2 at 60°. Cell U_5. Resistance, 23,000 ohms. Manometer 5. Calc. gas pressure, 24.450 atms. Time of setting up cell, March 18, 1912. Barometer during final record: max., 1.014; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 22,	26.234	Mar. 26,	26.276	Mar. 30,	26.281
23,	26.234	27,	26.287	31,	26.321
24,	26.234	28,	26.283	Apr. 1,	26.342
25,	26.256	29,	26.276		(11 days)

Mean total pressure, Mar. 22–Apr. 1 = 26.274 atms.
Mean barom. pressure, Mar. 22–Apr. 1 = 0.999 atm.
Mean osmot. pressure, Mar. 22–Apr. 1 = 25.275 atms.
Mean osmotic pressure for Expts. 1 and 2 = 25.2657 atms.
Ratio of osmotic to gas pressure = 1.0334

Table C

0.9 Wt. normal solution. Expt. 1 at 70°. Cell F_5. Resistance, 19,100 ohms. Manometer 24. Calc. gas pressure, 25.186 atms. Time of setting up cell, April 19, 1912. Barometer during final record: max., 1.016; min., 0.984. Total daily pressures:

Preliminary Record

	Atms.		Atms.		Atms.
Apr. 20,	28.709	Apr. 24,	26.145	Apr. 28,	(not rec.)
21,	26.273	25,	26.113	29,	27.671
22,	26.689	26,	26.312	30,	27.040
23,	26.137	27,	27.688		(11 days)

Final Record

	Atms.		Atms.		Atms.
May 1,	26.543	May 4,	26.562	May 6,	26.549
2,	26.593	5,	26.523	7,	26.574
3,	26.556				(7 days)

Mean total pressure, May 1–7 = 26.557 atms.
Mean barom. pressure, May 1–7 = 0.998 atm.
Mean. osmot. pressure, May 1–7 = 25.559 atms.

Table CI

0.9 Wt. normal solution. Expt. 2 at 70°. Cell R_3. Resistance, 16,500 ohms. Manometer 28. Calc. gas pressure, 25.186 atms. Time of setting up cell, April 29, 1912. Barometer during final record: max., 1.002; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 3,	26.589	May 5,	26.565	May 7,	26.551
4,	26.590	6,	26.559		(5 days)

Mean total pressure, May 3–7 = 26.571 atms.
Mean barom. pressure, May 3–7 = 0.997 atm.
Mean osmot. pressure, May 3–7 = 25.574 atms.

Table CII

0.9 Wt. normal solution. Expt. 3 at 70°. Cell C_3. Resistance, 7,700 ohms. Manometer 1. Calc. gas pressure, 25.186 atms. Time of setting up cell, April 29, 1912. Barometer during final record: max., 1.002; min., 0.989. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 2,	26.552	May 4,	26.552	May 6,	26.563
3,	26.534	5,	25.564	7,	26.541

Mean total pressure, May 2–7 = 26.551 atms.
Mean barom. pressure, May 2–7 = 0.997 atms.
Mean osmot. pressure, May 2–7 = 25.554 atms.
Mean osmot. pressure for Expts. 1, 2 and 3 = 25.562 atms.
Ratio of osmotic to gas pressure = 1.015

Table CIII

0.9 Wt. normal solution. Expt. 1 at 80°. Cell E_3. Resistance, 10,000 ohms. Manometer 31. Calc. gas pressure, 25.921 atms. Time of setting up cell, May 23, 1912. Barometer during final record: max., 1.001; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 24,	26.905	May 26,	26.914	May 27,	26.919
25,	26.909				

Mean total pressure, May 24–27 = 26.912 atms.
Mean barom. pressure, May 24–27 = 0.997 atm.
Mean osmot. pressure, May 24–27 = 25.915 atms.

Table CIV

0.9 Wt. normal solution. Expt. 2 at 80°. Cell G_5. Resistance, 10,000 ohms. Manometer 5. Calc. gas pressure, 25.921 atms. Time of setting up cell, May 20, 1912. Barometer during final record: max., 1.001; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 23,	26.974	May 25,	26.909	May 27,	26.909
24,	26.933	26,	26.873		

Mean total pressure, May 23–27 = 26.920 atms.
Mean barom. pressure, May 23–27 = 0.998 atm.
Mean osmot. pressure, May 23–27 = 25.922 atms.
Mean osmotic pressure for Expts. 1 and 2 = 25.919 atms.
Ratio of osmotic to gas pressure = 1.000

Table CV

1.0 Wt. normal solution. Expt. 1 at 30°. Cell R_5. Resistance, 110,000 ohms. Manometer 9. Calc. gas pressure, 24.716 atms. Time of setting up cell, May 4, 1910. Barometer during final record: max., 0.998; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 7,	28.317	May 8,	28.206	May 9,	28.186

Mean total pressure, May 7–9 = 28.236 atms.
Mean barom. pressure, May 7–9 = 0.996 atm.
Mean osmot. pressure, May 7–9 = 27.240 atms.

Table CVI

1.0 Wt. normal solution. Expt. 2 at 30°. Cell Z_5. Resistance, 300,000 ohms. Manometer 9. Calc. gas pressure, 24.716 atms. Time of setting up cell, May 11, 1910. Barometer during final record: max., 1.011; min., 0.993. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 12,	28.219	May 15,	28.227	May 17,	28.212
13,	28.212	16,	28.206	18,	28.227
14,	28.212				

Mean total pressure, May 12–18 = 28.2164 atms.
Mean barom. pressure, May 12–18 = 1.001 atms.
Mean osmot. pressure, May 12–18 = 27.2154 atms.

Table CVII

1.0 Wt. normal solution. Expt. 3 at 30°. Cell F_5. Resistance, 147,000 ohms. Manometer 9. Calc. gas pressure, 24.716 atms. Time of setting up cell, May 18, 1910. Barometer during final record: max., 1.000; min., 0.992. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 19,	28.227	May 21,	28.250	May 23,	28.242
20,	28.234	22,	28.242		

Mean total pressure, May 19–23 = 28.239 atms.
Mean barom. pressure, May 19–23 = 0.996 atm.
Mean osmot. pressure, May 19–23 = 27.242 atms.

Table CVIII

1.0 Wt. normal solution. Expt. 4 at 30°. Cell G_5. Resistance, 140,000 ohms. Manometer 15. Calc. gas pressure, 24.716 atms. Time of setting up cell, December 13, 1910. Barometer during final record: max., 1.012; min., 0.987. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Dec. 15,	28.205	Dec. 16,	28.215	Dec. 17,	28.192

Mean total pressure, Dec. 15–17 = 28.203 atms.
Mean barom. pressure, Dec. 15–17 = 1.007 atms.
Mean osmot. pressure, Dec. 15–17 = 27.196 atms.
Mean osmotic pressure for Expts. 1, 2, 3 and 4 = 27.2234 atms.
Ratio of osmotic to gas pressure = 1.101

Table CIX

1.0 Wt. normal solution. Expt. 1 at 40°. Cell B_5. Resistance, 150,000 ohms. Manometer 20. Calc. gas pressure, 25.533 atms. Time of setting up cell, March 9, 1910. Barometer during final record: max., 1.005; min., 0.996. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 10,	28.697	Mar. 11,	28.641	Mar. 12,	28.687

Mean total pressure, Mar. 10–12 = 28.675 atms.
Mean barom. pressure, Mar. 10–12 = 1.002 atms.
Mean osmot. pressure, Mar. 10–12 = 27.673 atms.

Table CX

1.0 Wt. normal solution. Expt. 2 at 40°. Cell R_3. Resistance, 110,000 ohms. Manometer 9. Calc. gas pressure, 25.533 atms. Time of setting up cell, June 3, 1910. Barometer during final record: max., 1.004; min., 0.992. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
June 5,	28.785	June 7,	28.732	June 9,	28.725
6,	28.739	8,	28.732	10,	28.732

Mean total pressure, June 5–10 = 28.741 atms.
Mean barom. pressure, June 5–10 = 0.998 atm.
Mean osmot. pressure, June 5–10 = 17.743 atms.

Table CXI

1.0 Wt. normal solution. Expt. 3 at 40°. Cell F_3. Resistance, 112,000 ohms. Manometer 5. Calc. gas pressure, 25.533 atms. Time of setting up cell, January 27, 1911. Barometer during final record: max., 1.008; min., 0.987. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Feb. 1,	28.695	Feb. 3,	28.684	Feb. 4,	28.721
2,	28.639				

Mean total pressure, Feb. 1–4 = 28.685 atms.
Mean barom. pressure, Feb. 1–4 = 0.997 atm.
Mean osmot. pressure, Feb. 1–4 = 27.688 atms.
Mean osmotic pressure for Expts. 1, 2 and 3 = 27.701 atms.
Ratio of osmotic to gas pressure = 1.085.

Table CXII

1.0 Wt. normal solution. Expt. 1 at 50°. Cell R_4. Resistance, 55,000 ohms. Manometer 9. Calc. gas pressure, 26.350 atms. Time of setting up cell, June 17, 1910. Barometer during final record: max., 0.996; min., 0.991. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
June 18,	29.194	June 21,	29.178	June 23,	29.230
19,	29.177	22,	29.193	24,	29.194
20,	29.186				

Mean total pressure, June 18–24 = 29.193 atms.
Mean barom. pressure, June 18–24 = 0.994 atm.
Mean osmot. pressure, June 18–24 = 28.199 atms.

Table CXIII

1.0 Wt. normal solution. Expt. 2 at 50°. Cell P_8. Resistance, 110,000 ohms. Manometer 29. Calc. gas pressure, 26.350 atms. Time of setting up cell, November 15, 1911. Barometer during final record: max., 1.008; min., 0.977. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 17,	29.230	Nov. 21,	29.225	Nov. 25,	29.213
18,	29.228	22,	29.221	26,	29.209
19,	29.250	23,	29.240	27,	29.213
20,	29.236	24,	29.243		(11 days)

Mean total pressure, Nov. 17–27 = 29.228 atms.
Mean. barom. pressure, Nov. 17–27 = 0.997 atm.
Mean osmot. pressure, Nov. 17–27 = 28.231 atms.

Table CXIV

1.0 Wt. normal solution. Expt. 3 at 50°. Cell E_8. Resistance, 62,000 ohms. Manometer 5. Calc. gas pressure, 26.350 atms. Time of setting up cell, November 18, 1911. Barometer during final record: max., 1.008; min., 0.984. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Nov. 23,	29.130	Nov. 27,	29.218	Dec. 1,	29.224
24,	29.153	28,	29.211	2,	29.211
25,	29.164	29,	29.218	3,	29.211
26,	29.150	30,	29.164	4,	29.224
					(12 days)

Mean total pressure, Nov. 23–Dec. 4 = 29.190 atms.
Mean barom. pressure, Nov. 23–Dec. 4 = 0.994 atm.
Mean osmot. pressure, Nov. 23–Dec. 4 = 28.196 atms.
Mean osmotic pressure for Expts. 1, 2 and 3 = 28.213 atms.
Ratio of osmotic to gas pressure = 1.071

Table CXV

1.0 Wt. normal solution. Expt. 1 at 60°. Cell W_5. Resistance, 3,200 ohms. Manometer 11. Calc. gas pressure, 27.167 atms. Time of setting up cell, March 21, 1911. Barometer during final record: max., 1.005; min., 0.977. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 24,	29.358	Mar. 28,	29.339	Mar. 31,	29.371
25,	29.298	29,	29.371	Apr. 1,	29.380
26,	29.309	30,	29.439	2,	29.358
27,	29.282				(10 days)

Mean total pressure, Mar. 24–Apr. 2 = 29.351 atms.
Mean barom. pressure, Mar. 24–Apr. 2 = 0.994 atm.
Mean osmot. pressure, Mar. 24–Apr. 2 = 28.357 atms.

Table CXVI

1.0 Wt. normal solution. Expt. 2 at 60°. Cell L_3. Resistance, 30,000 ohms. Manometer 5. Calc. gas pressure, 27.167 atms. Time of setting up cell, March 25, 1911. Barometer during final record: max., 1.012; min., 0.976. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Mar. 29,	29.319	Apr. 2,	29.377	Apr. 6,	29.399
30,	29.353	3,	29.405	7,	29.399
31,	29.331	4,	29.383	8,	29.421
Apr. 1,	29.358	5,	29.377		(11 days)

Mean total pressure, Mar. 29–Apr. 8 = 29.375 atms.
Mean barom. pressure, Mar. 29–Apr. 8 = 0.999 atm.
Mean osmot. pressure, Mar. 29–Apr. 8 = 28.376 atms.
Mean osmotic pressure for Expts. 1 and 2 = 28.3665 atms.
Ratio of osmotic to gas pressure = 1.044

Table CXVII

1.0 Wt. normal solution. Expt. 1 at 70°. Cell G_3. Resistance, 30,000 ohms. Manometer 28. Calc. gas pressure, 27.984 atms. Time of setting up cell, April 15, 1912. Barometer during final record: max., 1.016; min., 0.983. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 19,	29.542	Apr. 22,	29.630	Apr. 25,	29.589
20,	29.558	23,	29.591	26,	29.607
21,	29.599	24,	29.585	27,	29.610

Mean total pressure, Apr. 19–27 = 29.590 atms.
Mean barom. pressure, Apr. 19–27 = 1.000 atm.
Mean osmot. pressure, Apr. 19–27 = 28.590 atms.

Table CXVIII

1.0 Wt. normal solution. Expt. 2 at 70°. Cell L_2. Resistance, 33,000 ohms. Manometer 5. Calc. gas pressure, 27.984 atms. Time of setting up cell, April 15, 1912. Barometer during final record: max., 1.016; min., 0.983. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 17,	29.676	Apr. 21,	29.720	Apr. 25,	29.617
18,	29.623	22,	29.715	26,	29.646
19,	29.720	23,	29.635	27,	29.629
20,	29.746	24,	29.618		(11 days)

Mean total pressure, April 17–27 = 29.668 atms.
Mean barom. pressure, April 17–27 = 0.997 atm.
Mean osmot. pressure, April 17–27 = 28.671 atms.

Table CXIX

1.0 Wt. normal solution. Expt. 3 at 70°. Cell E_3. Resistance, 20,000 ohms. Manometer 1. Calc. gas pressure, 27.984 atms. Time of setting up cell, April 15, 1912. Barometer during final record: max., 1.016; min., 0.983. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 18,	29.572	Apr. 22,	29.617	Apr. 25,	29.587
19,	29.602	23,	29.610	26,	29.646
20,	29.602	24,	29.590	27,	29.632
21,	29.602				(10 days)

Mean total pressure, April 18–27 = 29.606 atms.
Mean barom. pressure, April 18–27 = 0.999 atms.
Mean osmot. pressure, April 18–27 = 28.607 atms.

Table CXX

1.0 Wt. normal solution. Expt. 4 at 70°. Cell R_4. Resistance, 33,000 ohms. Manometer 15. Calc. gas pressure, 27.984 atms. Time of setting up cell, April 15, 1912. Barometer during final record: max., 1.016; min., 0.983. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
Apr. 18,	29.608	Apr. 22,	29.628	Apr. 25,	2.9596
19,	29.628	23,	29.600	26,	29.647
20,	29.635	24,	29.590	27,	29.700
21,	29.621				(10 days)

Mean total pressure, April 18–27 = 29.625 atms.
Mean barom. pressure, April 18–27 = 0.999 atm.
Mean osmot. pressure, April 18–27 = 28.626 atms.
Mean osmotic pressure for Expts. 1, 2, 3 and 4 = 28.6235 atms.
Ratio of osmotic to gas pressure = 1.0228

Table CXXI

1.0 Wt. normal solution. Expt. 1 at 80°. Cell H_1. Resistance, 10,500 ohms. Manometer 31. Calc. gas pressure, 28.801 atms. Time of setting up cell, May 27, 1912. Barometer during final record: max., 1.000; min., 0.986. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 28,	29.838	May 30,	29.801	May 31,	29.780
29,	29.811				

Mean total pressure, May 27–31 = 29.808 atms.
Mean barom. pressure, May 27–31 = 0.992 atm.
Mean osmot. pressure, May 27–31 = 28.816 atms.

Table CXXII

1.0 Wt. normal solution. Expt. 2 at 80°. Cell L_n. Resistance, 10,000 ohms. Manometer 1. Calc. gas pressure, 28.801 atms. Time of setting up cell, May 27, 1912. Barometer during final record: max., 1.002; min., 0.993. Total daily pressures:

Final Record

	Atms.		Atms.		Atms.
May 31,	29.770	June 3,	29.799	June 6,	29.859
June 1,	29.863	4,	29.785	7,	29.799
2,	29.836	5,	29.829		

Mean total pressure, May 31–June 7 = 29.8175 atms.
Mean barom. pressure, May 31–June 7 = 0.998 atm.
Mean osmot. pressure, May 31–June 7 = 28.8195 atms.
Mean osmotic pressure for Expts. 1 and 2 = 28.8178 atms.
Ratio of osmotic to gas pressure = 1.000

Table CXXIII

0.1 Wt. Normal Sol.

30°

	Atms.
No. 1,	2.4756
2,	2.4721
3,	2.4682
4,	2.4796
Mean,	2.474
Ratio,	1.000

40°

	Atms.
No. 1,	2.5546
2,	2.5616
3,	2.5630
Mean,	2.5597
Ratio,	1.003

50°

	Atms.
No. 1,	2.643
2,	2.6338
3,	2.629
Mean,	2.6353
Ratio,	1.000

60°

	Atms.
No. 1,	2.7202
2,	2.7142
Mean,	2.7172
Ratio,	1.000

50°

	Atms.
No. 1,	5.2733
2,	5.2850
3,	5.2770
Mean,	5.2784
Ratio,	1.0016

0.2 Wt. Normal Sol.

30°

	Atms.
No. 1,	5.0397
2,	5.0478
Mean,	5.0438
Ratio,	1.020

60°

	Atms.
No. 1,	5.450
2,	5.4246
Mean,	5.4373
Ratio,	1.0008

40°

	Atms.
No. 1,	5.168
2,	5.158
Mean,	5.163
Ratio,	1.011

0.3 Wt. Normal Sol.

30°

	Atms.
No. 1,	7.6409
2,	7.6526
Mean,	7.6468
Ratio,	1.031

Table CXXIII—(Continued)

40°	Atms.
No. 1,	7.817
2,	7.853
3,	7.831
4,	7.835
Mean,	7.844
Ratio,	1.024

50°	Atms.
No. 1,	7.960
2,	7.9879
3,	7.9737
Mean,	7.9739
Ratio,	1.0087

60°	Atms.
No. 1,	8.1522
2,	8.1283
Mean,	8.1403
Ratio,	0.999

0.4 Wt. Normal Sol.

30°	Atms.
No. 1,	10.305
2,	10.285
Mean,	10.295
Ratio,	1.040

40°	Atms.
No. 1,	10.599
2,	10.6025
3,	10.6067
4,	10.5864
Mean,	10.5987
Ratio,	1.0377

50°	Atms.
No. 1,	10.737
2,	10.710
Mean,	10.724
Ratio,	1.017

60°	Atms.
No. 1,	10.871
2,	10.853
3,	10.873
Mean,	10.866
Ratio,	1.000

0.5 Wt. Normal Sol.

30°	Atms.
No. 1,	12.9804
2,	12.9754
Mean,	12.9779
Ratio,	1.050

40°	Atms.
No. 1,	13.349
2,	13.361
Mean,	13.355
Ratio,	1.046

50°	Atms.
No. 1,	13.5148
2,	13.4927
3,	13.5037
Mean,	13.5037
Ratio,	1.025

60°	Atms.
No. 1,	13.645
2,	13.6873
Mean,	13.6662
Ratio,	1.006

70°	Atms.
No. 1,	13.991
2,	13.990
Mean,	13.9905
Ratio,	1.000

0.6 Wt. Normal Sol.

30°	Atms.
No. 1,	15.706
2,	15.6937
3,	15.763
4,	15.690
Mean,	15.7132
Ratio,	1.0595

40°	Atms.
No. 1,	16.137
2,	16.154
Mean,	16.146
Ratio,	1.054

50°	Atms.
No. 1,	16.322
2,	16.306
Mean,	16.319
Ratio,	1.032

Table CXXIII—(Continued)

60°

	Atms.
No. 1,	16.519
2,	16.551
Mean,	16.535
Ratio,	1.014

70°

	Atms.
No. 1,	16.815
2,	16.824
Mean,	16.8195
Ratio,	1.0018

0.7 Wt. Normal Sol.

30°

	Atms.
No. 1,	18.4937
2,	18.5046
Mean,	18.4992
Ratio,	1.069

40°

	Atms.
No. 1,	18.962
2,	18.901
Mean,	18.932
Ratio,	1.0592

50°

	Atms.
No. 1,	19.2245
2,	19.1794
Mean,	19.2019
Ratio,	1.041

60°

	Atms.
No. 1,	19.4028
2,	19.4046
Mean,	19.4037
Ratio,	1.020

70°

	Atms.
No. 1,	19.553
2,	19.583
Mean,	19.568
Ratio,	0.999

0.8 Wt. Normal Sol.

30°

	Atms.
No. 1,	21.396
2,	21.354
Mean,	21.375
Ratio,	1.081

40°

	Atms.
No. 1,	21.779
2,	21.813
3,	21.819
4,	21.811
Mean,	21.8028
Ratio,	1.0674

50°

	Atms.
No. 1,	22.1285
2,	22.1035
Mean,	22.116
Ratio,	1.049

60°

	Atms.
No. 1,	22.344
2,	22.310
Mean,	22.327
Ratio,	1.027

70°

	Atms.
No. 1,	22.567
2,	22.567
Mean,	22.567
Ratio,	1.008

80°

	Atms.
No. 1,	23.062
Ratio,	1.001

0.9 Wt. Normal Sol.

30°

	Atms.
No. 1,	24.2146
2,	24.238
Mean,	24.2263
Ratio,	1.089

40°

	Atms.
No. 1,	24.738
2,	24.730
3,	24.738
Mean,	24.735
Ratio,	1.076

50°

	Atms.
No. 1,	25.132
2,	25.1136
Mean,	25.1228
Ratio,	1.0593

Table CXXIII—(Continued)

1.0 Wt. Normal Sol.

60°		30°		60°	
	Atms.		Atms.		Atms.
No. 1,	25.2564	No. 1,	27.240	No. 1,	28.357
2,	25.275	2,	27.2154	2,	28.376
Mean,	25.2657	3,	27.242	Mean,	28.3665
Ratio,	1.0334	4,	27.196	Ratio,	1.044
		Mean,	27.2234		
		Ratio,	1.101		

70°		40°		70°	
	Atms.		Atms.		Atms.
No. 1,	25.559	No. 1,	27.673	No. 1,	28.590
2,	25.574	2,	27.743	2,	28.671
3,	25.554	3,	27.688	3,	28.607
Mean,	25.562	Mean,	27.701	4,	28.626
Ratio,	1.015	Ratio,	1.085	Mean,	28.6235
				Ratio,	1.0228

80°		50°		80°	
	Atms.		Atms.		Atms.
No. 1,	25.915	No. 1,	28.199	No. 1,	28.816
2,	25.922	2,	28.231	2,	28.8195
Mean,	25.919	3,	28.196	Mean,	28.8178
Ratio,	1.000	Mean,	28.213	Ratio,	1.000
		Ratio,	1.071		

Table CXXIV

Weight-normal concentration

Mean osmotic pressure in atmospheres

Temp.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0°	(2.462)	4.722	7.085	9.442	11.895	14.381	16.886	19.476	22.118	24.825
5°	2.452	4.818	7.198	9.608	12.100	14.605	17.206	19.822	22.478	25.283
10°	2.498	4.893	7.334	9.790	12.297	14.855	17.503	20.161	22.884	25.693
15°	2.541	4.985	7.476	9.949	12.549	15.144	17.815	20.535	23.305	26.189
20°	2.590	5.064	7.605	10.137	12.748	15.388	18.128	20.905	23.717	26.638
25°	2.634	5.148	7.729	10.296	12.943	15.624	18.434	21.252	24.126	27.053
30°	2.474	5.044	7.647	10.295	12.978	15.713	18.499	21.375	24.226	27.223
40°	2.560	5.163	7.844	10.599	13.355	16.146	18.932	21.803	24.735	27.701
50°	2.635	5.278	7.974	10.724	13.504	16.319	19.202	22.116	25.123	28.213
60°	2.717	5.437	8.140	10.866	13.666	16.535	19.404	22.327	25.266	28.367
70°	...	...	...	....	13.991	16.820	19.568	22.567	25.562	28.624
80°	...	...	...	....	....	....	....	23.062	25.919	28.000
90°	...	...	...	....	....	....	....	....	....	....
100°	...	...	...	....	....	....	....	....	....	....

Table CXXV

Weight-normal concentration

Temp.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	Ratio of osmotic to gas pressure									
0°	(1.106)	1.061	1.061	1.060	1.069	1.077	1.083	1.093	1.104	1.115
5°	1.082	1.063	1.058	1.059	1.067	1.074	1.084	1.093	1.102	1.115
10°	1.082	1.060	1.059	1.060	1.066	1.073	1.083	1.092	1.102	1.113
15°	1.082	1.061	1.061	1.059	1.068	1.073	1.083	1.093	1.102	1.115
20°	1.084	1.062	1.060	1.060	1.067	1.073	1.084	1.093	1.103	1.115
25°	1.084	1.059	1.060	1.059	1.065	1.071	1.083	1.093	1.102	1.113
	(1.083)	(1.061)	(1.060)	(1.060)	(1.067)	(1.074)	(1.083)	(1.093)	(1.103)	(1.114)
30°	1.000	1.020	1.031	1.040	1.050	1.060	1.069	1.081	1.089	1.101
40°	1.003	1.011	1.024	1.038	1.046	1.054	1.059	1.067	1.076	1.085
50°	1.000	1.002	1.009	1.017	1.025	1.032	1.041	1.049	1.059	1.071
60°	1.000	1.001	0.999	1.000	1.006	1.015	1.020	1.027	1.033	1.044
70°	...	...	...	...	1.000	1.002	0.999	1.008	1.015	1.023
80°	...	...	...	...	...	...	...	1.001	1.000	1.000
90°	...	...	...	...	...	...	...	...	...	...
100°	...	...	...	...	...	...	...	...	...	...

Tables II to CXXII, inclusive, give somewhat detailed records of the individual experiments.

Table CXXIII contains, for each concentration of solution and each temperature, the observed osmotic pressures, their mean values, and the ratios of osmotic to calculated gas pressures. It is recalled in this connection—for the information of those who are not familiar with the earlier papers—that the standard for the calculation of the gas pressure of the solute is *not* the volume of the solution, *but the volume of the solvent in pure condition and at the temperature of maximum density, i. e., at 4° C.* It is to be noted, also, that the value $0.00367t$ has been employed in all calculations of pressure; hence, in so far as this coefficient is incorrect for nitrogen gas at the higher pressures, a correction is still to be applied to the osmotic pressures which are recorded in the tables.

Table CXXIV gives, for each of the 10 concentrations of solution, the osmotic pressures which have been found between 0° and the highest temperature at which we have worked up to the present time. This "highest temperature" was 60° for the 0.1, 0.2, 0.3 and 0.4 weight-normal solutions; 70° for the 0.5, 0.6 and 0.7 weight-normal concentrations; and 80° for the 0.8, 0.9 and 1.0 normal solutions. The work between 0° and 25° was reported in our last paper,[1] but is included in order that the pressures at the lower temperatures may be readily compared with those which were observed at the higher temperatures.

In Tables CXXV the osmotic pressure given in Table CXXIII are stated in the more convenient form of ratios of osmotic to gas pressure.

The obvious conclusions to be drawn from Table CXXV are:

1. Between 0° and 25°, all concentrations of cane sugar solutions, from 0.1 to 1.0 weight-normal, obey strictly the law of Gay-Lussac for gases. The same is true of the 0.1 normal solution between 30° and 60°, and of the 0.2 normal solution between 50° and 60°. In all of the cases cited the

[1] This Journal, **48**, 554.

ratio of osmotic to gas pressure is constant within the specified ranges of temperature.

2. Between 25° and 30°, the ratio of osmotic to gas pressure (which is constant, but greater than unity from 0° to 25°) begins to decline in all concentrations, but relatively more rapidly in the more dilute solutions.

3. The decline in ratio, which begins between 25° and 30°, continues at the higher temperatures until osmotic pressure becomes, in every instance, equal to the calculated gas pressure of the solute. It is not yet obvious whether the unit ratio, once reached, will be maintained at all higher temperatures; but the conduct of the 0.1 normal solution between 30° and 60°, and of the 0.2 normal solution between 50° and 60°, throws some light upon this important question.

4. The law of Boyle will be found to hold in four cases in Table CXXV; namely: (1) in that of the 0.1 and 0.2 normal solutions at 50°; (2) in that of the 0.1, 0.2, 0.3 and 0.4 normal solutions at 60°; (3) in that of the 0.5, 0.6, and 0.7 normal solutions at 70°; and (4) in the case of the 0.8, 0.9 and 1.0 normal solutions at 80°. On the other hand, there is nowhere to be found in the table any convincing evidence that the law of Boyle does not hold for osmotic pressure.

The blank spaces in Tables CXXIV and CXXV indicate the field which we hope to investigate during the coming year, but it is by no means certain that we shall be able to carry on the work at temperatures much above 80°. At this temperature, and even at 70°, the accurate measurement of osmotic pressure is costly and enormously difficult. The following statement will serve to illustrate its costliness. The measurement of osmotic pressure at 30° was begun with an equipment of 16 manometers, the preparation of which has cost us more than a year's labor—the average time required for the complete investigation of a manometer being about one month. During the course of the work between 60° and 80°, 12 of these instruments were put out of commisssion, half of them permanently.

JOHNS HOPKINS UNIVERSITY,
June, 1912

REVIEWS

COCOA AND CHOCOLATE, THEIR CHEMISTRY AND MANUFACTURE. By R. WHYMPER. Philadelphia: P. Blakiston's Son & Co. 1912. pp. xi + 327. Price, $5.00.

In this exhaustive English work the author states that "for the first time the chemical composition of cocoa has been traced from the fresh beans through the various stages of manufacture, so that the changes which occur during fermentation, drying, roasting, etc., may be followed." The subject is divided into three parts, dealing respectively with the history, botany, and agriculture of cocoa; manufacture of chocolates and cocoa powders; chemistry of cocoa. The history and growth of the cocoa industry is written in a very interesting and informing manner, being traced from the days of Cortes. Some startling figures are presented to show the phenomenal growth of this industry. For the decade ending 1908, the consumption of coffee in the United Kingdom remained practically stationary, while that of cocoa increased from 39,000,000 to 57,000,000 pounds per annum. For the year ending June 30, 1909, the United States was at the head of all cocoa-consuming countries, 130,000,000 pounds of cocoa being used during that period. A brief chapter is given to the botany and nomenclature of the different varieties of cocoa. Discussing the agriculture of cocoa, the author treats of such important features as selection of site, soil, manure and seed, and describes the best methods of planting and of combating various diseases, together with observations upon pruning and picking. Information on this subject appears to be comprehensive and practical and should be of great value to those intending to engage in the culture of cocoa. The great importance of properly fermenting the beans is emphasized and tables of analyses are given to show what changes occur in cocoa beans during this process. Washing, drying and polishing follow the fermentation.

The characteristics of the principal kinds of commercial cocoa beans are then discussed, together with the output of each. The author then deals with the composition of raw cocoa beans, giving tables of analyses from well known workers in this field. Various details of the manufacture of chocolates and cocoa powders are faithfully presented, illustrated by photographs of the modern machinery now in use. Analyses of the bean before and after roasting are given to show what changes take place during this process, and subsequent tables to illustrate losses and changes sustained by the beans at

other stages of their passage through the factory. So-called soluble cocoa powders are discussed and the different methods of the application of alkali in preparing these are presented in detail. This is followed by analyses of various commercial cocoa powders and a discussion of interpretation of results of analysis of these products. The preparation of chocolate and various chocolate products, together with analyses of the same, is taken up in a thorough manner and many receipts for making these preparations are given. This part of the book dealing with the various manufacturing processes now in use is exhaustive and modern in its treatment of this phase of the subject. Part III, which concerns itself with the chemistry of cocoa, begins with a survey of the component parts of roasted cocoa beans, dealing first with the husk and then with the nibs. The different constituents of both are treated in a scientific way and many tables of analyses are given to support the text. In a similar manner the component parts of cocoa powders, chocolate and milk chocolates are treated. A short chapter on microscopical examination of cocoa preparations describes the normal appearance of cocoa under the microscope, and discusses the various adulterants which may be expected. In the chapters on methods of analysis, the author discusses the most recent methods and recommends only those which he himself has found to give accurate results. This resolution seems to have been followed and the methods appearing are mostly those which deserve a place in such a book.

The author is not quite correct, however, in stating that a modification of the Kunze and Decker method for xanthine bases, and the Dubois method for the determination of lactose and sucrose in milk chocolate, are recommended by the A. O. A. C. These methods have only been adopted as provisional by the association and subsequent work proved the latter less reliable than at first supposed, so that it has not been adopted as an official method. The form in which the method is now before the association for consideration prior to official adoption is materially different from that which was originally presented, in that the polarization at 87° for the determination of lactose is discontinued, calculation of this constituent being made entirely from the same polarizations as are used in the sucrose calculation.

Following the chapters on methods are the provisional definitions and standards of cocoa preparations adopted at the Congress of Cocoa and Chocolate Makers, held at Byrne in August, 1911, and a bibliography of some of the more important literature on the subject. The book as a whole is excellent and is a valuable addition to the literature upon the

subject and should prove of great assistance to those working in this field. W. L. DUBOIS

DIE ELEKTROCHEMISCHEN VERFAHREN DER CHEMISCHEN GROSS-INDUSTRIE, ihre Prinzipien und ihre Ausführung. Von DR. JEAN BILLITER, Privatdozent an der Universität Wien. II Band: Elektrolysen mit unlöslichen Anoden ohne Metallabscheidung. Mit 228 Figuren und 53 Tabellen im Text und einem Anhang: Neuerungen der letzten Zeit auf dem Gesamtgebiete der technischen Elektrolyse wässriger Lösungen. Mit 9 Figuren im Text. Halle a. S.: Verlag von Wilhelm Knapp. 1911. pp. ix + 535. Price, M. 28.50.

The author contemplates writing a treatise of four volumes which is to cover the whole field of electrochemical endeavor. In 1909 he brought out Vol. I,[1] which dealt with the electrodeposition of metals from aqueous solutions, using principally soluble anodes. The present volume discusses electrolytic processes in which no metal is plated out, and the anodes used are mainly insoluble. The remaining two volumes are to treat of pyroelectrolytic and electrothermic processes. The subject of the volume under consideration is taken up under the three main heads, electrolysis of water, of chloride solutions, and of bromide solutions. There is added an appendix in which are brought together the improvements in the electrodeposition of metals which have been published since 1909, as well as those relating to the subject of Vol. II which have become known since the manuscript went to press. The whole subject is thus brought to date of publication.

The author has discussed principles and practice. Principles are common property, practice is not. In treating the latter a writer is at a great disadvantage in that most of the electrolytic plants do not allow descriptions of apparatus to be published nor any information to be given out. Most of the illustrations in the book therefore have to be diagrammatic sketches, reproductions of patent specifications, or some other form of general illustration, which explains the principles, but omits the important details. This discussion of practice is unfortunate, but cannot be helped under the prevailing policy of secrecy which seems to be increasing in electrolytic lines. The author has done as well as could be expected, he has given clear expositions of principles, and illustrated the practice in a general way as far as information was available. The reader who knows the full details of one process or another will find the descriptions inadequate, but he will profit by the general discussion of this process which may furnish a better general view than the specialist possesses. The book is a welcome addition to the technical literature. H. O. HOFMAN

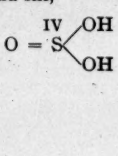
[1] THIS JOURNAL, **43**, 472.

DAS HYDROSULFIT. Teil I. Grundzüge der physikalischen Chemie des Hydrosulfits im Vergleich zu analogen Schwefelsauerstoffderivaten. Von DR. KARL JELLINEK, PH.D., Privatdozent an der Technischen Hochschule zu Danzig. Mit 15 Kurven. Sammlung chemischer und chemisch-technischer Vorträge, begründet von F. B. AHRENS, herausgegeben von PROF. DR. W. HERZ, Breslau. XVII Band. 1–5 Heft. Stuttgart: Verlag von Ferdinand Enke. 1911. Price, M. 6.

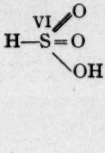
This is the first book which has been written to illustrate the application of the principles of theoretical chemistry in the case of a typical reducing agent, hydrosulphite. It should prove as valuable to advanced students of chemistry as Abel's well known book on a typical oxidizing agent, hypochlorite.

The principal topics discussed are as follows: Methods of analysis; the ordinary preparation of pure, stable, anhydrous hydrosulphite; the molecular formula; the constitution in comparison with that of other sulphur-oxygen compounds; aldehyde compounds of hydrosulphite; the constitutional formula; the heterogeneous equilibria in the binary system, H_2O–$Na_2S_2O_4$, including the determination of the transition point, $Na_2S_2O_4$–$Na_2S_2O_4 \cdot 2H_2O$; conductivity and ionization of the oxygen acids of sulphur, and of the sodium salts; calculation of the ionization constants of the acids from the conductivity data for these acids and for the acid salts, and from electromotive force measurements with a hydrogen electrode; electromotive force corresponding to the reaction $S_2O_4^{--} + 2H_2O = 2HSO_3^- + H_2$; the electrolytic preparation of hydrosulphite from sulphate. A second monograph is promised which will deal more in detail with the inorganic, organic and technical chemistry of hydrosulphite.

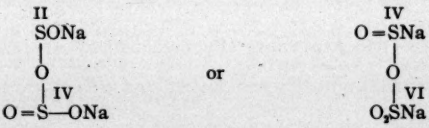
Much of the material here presented is based on the recent experimental work of a single investigator, the author, and some of the results may therefore be altered by future investigators. Furthermore, owing to the variety of theoretical subjects discussed, it is obvious that any chemist will be able to find specific instances in which he disagrees with the author's conclusions, or in which he would like to alter the method of presentation. The reviewer, for example, considers that the chapter on the constitution of sulphur-oxygen compounds would be much improved by the introduction of the idea of positive and negative valences already adopted by so many chemists. The author has assigned to sulphur in the symmetric and asymmetric forms of sulphurous acid the valences four and six,



and



but would it not be much simpler to consider that in each case the valence of sulphur is +4? The latter method has the advantage that each process of oxidation corresponds to a definite increase of the positive valence or to a definite decrease of the negative valence of some element, and that the equation for any oxidation-reduction reaction may be written at once when the initial and final substances are known. The average valence of sulphur in sodium hydrosulphite is +3, but the author presents evidence to show that the formula is either



from which it is evident that the valences of the sulphur atoms are +2 and +4, respectively. WILLIAM C. BRAY

STAND UND WEGE DER ANALYTISCHEN CHEMIE. Von PROF. DR. WILHELM BÖTTGER, Universität Leipzig. Die chemische Analyse: Sammlung von Einzeldarstellungen auf dem Gebiete der chemischen, technisch-chemischen und physikalisch-chemischen Analyse, herausgegeben von DR. B. M. MARGOSCHES, Privatdozent an der Deutschen Technischen Hochschule Brünn. XIII Band. Stuttgart: Verlag von Ferdinand Enke. 1911. pp. 55. Price, M. 1.80.

This interesting brochure deals with the present status of analytical chemistry as an art and as a branch of chemical science in a spirit of intelligent criticism which is most helpful and enlightening. The author writes from the viewpoint of one well informed regarding the advances of the science in physico-chemical fields, as well as that of one who is himself skilled in the operations and versed in the processes of analytical chemistry. His acquaintance with conditions prevailing in this country, as a consequence of his residence here, lend added value to his comments, and his evident appreciation of the work of Dr. W. F. Hillebrand should enlist the sympathy of American readers.

Dr. Böttger deplores the present subordinate position of analytical chemistry and the general defectiveness of much of the published work of chemical analysts, and also their indisposition to avail themselves of the aids which are now available from other branches of chemical science. This he ascribes in part to the faulty instructional methods, to the discussion of which he devotes a chapter of his monograph. In separate chapters he points out how the processes of gravimetric and volumetric analysis may be made more exact,

and may be scientifically investigated by taking advantages of facts and principles which are the products of modern chemical research. As an appendix he gives a translation of Dr. Hillebrand's address entitled "Some Thoughts on the Present Condition of Analytical Chemistry," delivered in 1905, which is hardly less applicable to-day than at the time of its delivery.

A perusal of this pamphlet is to be heartily commended to teachers, investigators, and especially to practitioners.

H. P. TALBOT

A HANDBOOK OF ORGANIC ANALYSIS, QUALITATIVE AND QUANTITATIVE. By HANS THATCHER CLARKE, B.Sc. (Lond.), A.I.C., Lecturer on Stereochemistry in University College, London. With an Introduction by J. NORMAN COLLIE, PH.D., LL.D., F.R.S., Professor of Organic Chemistry in University College, London. New York: Longmans, Green & Co. pp. viii + 264. Price, $1.40.

In the introduction to this book Professor Collie shows the need that exists for it in the following words: "Organic analysis, qualitative and quantitative, has of recent years acquired increasing importance in the training of the chemist. And this with reason, for the examination of unknown organic compounds has, perhaps, an even greater educational value than has that of inorganic substances.

"At the present time hardly any books exist which deal with the systematic testing of organic substances. There are many that describe the preparation of organic substances, give quantitative methods, and deal with special analysis of distinct classes of compounds. But the book that would enable the chemist to find out qualitatively the nature of the multitudinous carbon derivatives met with in ordinary work in an organic laboratory—that book is wanted.

"It is by no means easy to arrange a general plan for testing organic compounds so that one can say for certain what the particular compound may be. But as organic chemistry is an eminently practical science, there ought to be good practical books dealing with the subject—books where the descriptions are concise, where the treatment of the subject is systematic and not merely an enumeration of special tests for special compounds, and where the student has to use his head as well as the information supplied by the text-book. Mr. Clarke has in this book recognized these requirements."

Again Professor Collie says: "The most important novelty, however, in the book is to be found in the chapter 'Tables of Compounds.' In this chapter Mr. Clarke has collected together the data that are wanted by the ordinary student after he has determined as far as possible the nature of the

organic compound he is analyzing, i. e., the nature of the radicles present, its melting and boiling point, and possibly its molecular weight. Under ordinary conditions, after these data have been obtained, a lengthy hunt through a dictionary or manual of organic chemistry must be made to try to find what particular substance agrees with the facts discovered. In the 'Table of Compounds' a complete list is given of all the more important compounds to be met with, together with their properties, and thus much valuable time is gained through the possibility of making a direct comparison of the properties under investigation."

The first chapter is devoted to the preliminary investigation. The "Examination for Radicles" and "Separation of Organic Compounds" are the headings for Chapters Two and Three. Chapter Four contains the classified tables of common organic compounds, while Chapters Five and Six are given up to quantitative determinations of the constituent elements and radicals. Chapter Seven deals with the determination of some physical properties, such as molecular weight, vapor density, optical rotation, etc. There is an index of substances and also a good general index.

Mr. Clarke's book covers a great deal of ground and gives all that the average student should need. It will be of great assistance to any one testing organic substances, and will help to put quantitative organic chemistry on as systematic a basis as qualitative inorganic chemistry has been for many years.

W. R. O.

THE CHEMISTRY OF THE RADIO ELEMENTS. By FREDERICK SODDY, F.R.S., Lecturer in Physical Chemistry and Radioactivity in the University of Glascow. Monographs on Inorganic and Physical Chemistry. Edited by ALEXANDER FINDLAY, D.Sc. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1911. pp. 92. Price, $0.90.

It may be desirable to separate the chemistry of the radioactive elements from the physics of radioactivity. But when we consider how little we really know of the chemistry of these substances as such, this appears to the reviewer to be very doubtful. The fact is that we have thus far not been able to obtain enough of the more highly radioactive substances to study them profitably by chemical methods—physical methods, in general, requiring much less material than chemical.

The transformations of uranium, radium, thorium and actinium constitute the chief subjects treated in this little booklet.

H. C. J.

PHYSICO-CHEMICAL CALCULATIONS. By JOSEPH KNOX, D.Sc., Lecturer on Inorganic Chemistry, University of Aberdeen. London: Methuen & Co., Ltd. pp. viii + 188. Price, 2s. 6d.

This book is based on Abegg and Sackur's "Physikalisch-chemische Rechenaufgaben,"[1] but instead of simply giving a short summary of the laws and formulas used in the problems, as in the German book, the subject matter has been arranged in chapters dealing with the main subdivisions of physical chemistry and a short introduction appended to each chapter, treating of the theory involved in the problems. In this way, and by the addition of many new problems, the contents of Abegg and Sackur's book have been almost doubled. The book should serve excellently in showing the student how to apply practically the various principles and formulas which he learns in the theoretical study of physical chemistry.

C. A. R.

A TEXT-BOOK OF INORGANIC CHEMISTRY. By DR. A. F. HOLLEMAN, Professor Ordinarius in the University of Amsterdam. Issued in English in coöperation with HERMON CHARLES COOPER. Fourth English edition, completely revised. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1912. pp. viii + 505. Price, $2.50.

Prof. Cooper says in the Preface: "The present edition represents a thorough revision of the work of the Dutch author and the American collaborator. It profits by the author's experience with the frequent editions in other languages but is independent in composition.

"Very many of the descriptive portions have been rewritten, notably those on the sulphur oxides and acids, sodium hydroxide and carbonate, radioactive elements and platinum, as well as the sections on thermochemistry, colloids and the iron-carbon system, while the subjects of stability and the reality of molecules and atoms furnish new material."

This book is so well known that it is only necessary to call attention to the fact that a new edition has appeared.

C. A. R.

LES NOUVEAUTÉS CHIMIQUES POUR 1911. Nouveaux Appareils de Laboratoire, Méthodes Nouvelles de Recherches appliquées à la Science et à l'Industrie. Par CAMILLE POULENC, Docteur ès Sciences. Avec 178 figures intercalées dans le texte. Paris: Librairie J.-B. Baillière et Fils. 1911. pp. viii + 354. Price, Fr. 4.

The 1911 volume of this Annual contains the usual interesting collection of descriptions of new forms of apparatus designed for the use of physicists, chemists and bacteriologists. It is well worth while glancing through.

C. A. R.

[1] See THIS JOURNAL, **44**, 110.